THE TRANSPORT OF AEROSOLS INTO DENALI NATIONAL PARK AND PRESERVE

By

Ashley N. Wallace

RECOMMENDED:

Advisory Committee Chair

Chair, Department of Chemistry and Biochemistry

APPROVED:

Dean, College of Natural Science and Mathematics

Dean of the Graduate School

April 9, 2012

Date

THE TRANSPORT OF AEROSOLS INTO DENALI NATIONAL PARK AND PRESERVE

A

THESIS

Presented to the Faculty

of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

By

Ashley N. Wallace, B.S.

Fairbanks, Alaska

May 2012

Abstract

Denali National Park and Preserve (DNPP) is a federally protected Class I visibility area in Alaska. The Regional Haze Rule in the U.S. Clean Air Act requires the visibility in all Class I areas to be 'pristine.' According to the EPA DNPP does not have 'pristine' air. Therefore, the Alaska Department of Environmental Conservation conducted a 15-month study of particulate matter smaller than 2.5 micrometers ($PM_{2.5}$) from March, 2008 through June, 2009 to identify the aerosol sources in DNPP. DRUM aerosol impactors collected aerosols at four sites (DNPP Headquarters, Trapper Creek, McGrath, and Lake Minchumina) around DNPP. The aerosol data underwent a series of analyses including: a seasonal analysis of elemental composition, an analysis of potential source regions as identified by the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, and Chemical Mass Balance (CMB) analyses to identify specific aerosol sources. These analyses show that the predominant sources of aerosols impacting DNPP during winter and spring lie outside of Alaska and during summer and fall are from outside and local sources. Outside sources include deserts in China and industry in Russia. Because many of the aerosols impacting DNPP are produced internationally, the visibility in DNPP cannot be restored without international collaboration.

Table of Contents

Page

List of Figures

List of Tables

Acknowledgments

I would like to thank the staff of the Geophysical Institute of the University of Alaska Fairbanks for their assistance with this research. I would further like to thank Cathy Cahill for being my mentor throughout this research project and Drs. William Simpson and Nicole Mölders, for their guidance. I would also like to thank the IMPROVE (Interagency Monitoring of PROtected Visual Environments) monitoring program for providing data on aerosol concentrations (http://vista.cira.colostate.edu/improve/Default.htm), the NOAA Air Resources Laboratory for use of the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model for air parcel trajectories (http://www.arl.noaa.gov/ready/hysp_info.html), and the U.S. EPA for use of the Chemical Mass Balance (CMB) Model EPA-CMBv8.2 (http://www.epa.gov/scram001/receptor_cmb.htm). I would also like to thank Dr. J. G. Watson for his assistance with the Chemical Mass Balance model. This research was funded by the Alaska Department of Environmental Conservation and the University of Alaska Department of Chemistry and Biochemistry.

On a personal note I would also like to thank al of my friends and family who supported me mentally and emotionally throughout this endeavor. They have cheered me on through phone calls, Facebook™, e-mails, and lunch dates and I appreciate it so much to have their support through this.

In particular I would like to thank my parents, Fred and Dee Wallace, who supported me more than they will ever know, gave me words of wisdom and encouragement, and "knew I could do it" all along – even when I thought I couldn't. I

would also like to thank my husband Brian Edwards for also being there for me – through the "sunny days" and the "rainy days" - saying how proud he was of me and always keeping me laughing and smiling, just like he always has and always will.

Chapter 1

Introduction

Clean crisp air in an uncontaminated environment; that is what is generally thought of the state of national parks and wilderness areas in the United States. Alaska parks, in particular, are thought to be pristine because they are in the remote, thought to be clean Arctic. To keep the air in the national parks and wilderness areas clean, the 1990 federal Clean Air Act Amendments implemented a visibility protection program called the Regional Haze Rule. The Regional Haze Rule protects Class I areas from visibility impairment caused by anthropogenic pollution. A Class I area, as defined by the Clean Air Act, include national parks greater than 6,000 acres, wilderness areas and national memorial parks greater than 5,000 acres, and international parks that existed as of August 1977. Under the Regional Haze Rule Class I areas are required to reach a mandatory visibility 'value' of 'pristine'. There are four Class I areas in Alaska: Denali National Park and Preserve (DNPP), Tuxedni Wilderness Area, Bering Sea Wilderness Area, and Simeonof Wilderness Area (figure 1).

Figure 1. Class I Areas in Alaska (Air Resource Specialists, 1992).

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) air quality network was set up to measure the aerosol concentrations and compositions that are needed to identify sources of visibility degradation in Class I areas (Malm, 1994). There are two IMRPOVE monitoring stations representing DNPP, one at the DNPP headquarters and one at Trapper Creek, and one monitoring station each near the Tuxedni and Simeonof Wilderness Areas. The DNPP headquarters site was the first IMPROVE site in Alaska and began monitoring in 1988. The DNPP headquarters site was followed by the sites at Simeonof, Tuxedni, and Trapper Creek in 2001. The Bering Sea Wilderness Area does not have a monitoring station due to its remote location.

Results from the IMPROVE network and other aerosol measurements show that local aerosol sources emit aerosols into the Alaskan air. For example, forest fires emit

smoke during the summer forest fire season (Polissar, 1998a; Wilcox II, 2003; Cahill, 2008) and oceanic storms cause sea spray during winter (Polissar, 1998a; Shaw, 1988; Wilcox II, 2003). In addition, Alaskan aerosol measurements show that two key transport phenomenon bring aerosols to Alaska from distant sources (Malm, 1994; Polissar, 1998a; Polissar, 1998b; Shaw, 1995; Wilcox, 2003). The first of these phenomena is Arctic Haze (Shaw, 1995). Arctic Haze was first discovered in 1956 by an Air Force officer named Mitchell. He saw bands of a dark colored haze when he flew over the Arctic. Raatz (1984) analyzed data taken during military flights and found, according to the flight logs, that this haze occurred seasonally (mostly in late winter). He also deduced that this haze had to come from outside of Alaska since there were no sources of the haze inside Alaska. The first scientific studies of the sources of the aerosols making up the haze occurred in the late 1970s and early 1980s when programs such as the Arctic Gas and Aerosol Sampling Program (AGASP) examined the aerosols making up the haze (Rahn, 1977; Raatz, 1984; Schnell, 1984). These studies determined that Arctic Haze is made of anthropogenic pollutants such as sulfur/sulfate, vanadium, manganese, black carbon, and some heavy metals that enter Alaska from Eurasia during late winter and early spring (Shaw, 1988; Shaw, 1995; Wilcox II & Cahill, 2003).

The second transport phenomenon that brings aerosols from a distant source to Alaska is Asian dust (Rahn, 1977). An Asian dust event occurs when soil from the Gobi desert is transported from China to the northeast over the North Pacific Ocean and onto the North American continent, including Alaska (Wetzel, 2003). Asian dust aerosols

contain elements commonly found in soil and can have a large impact on visibility in Alaska (Cahill, 2003; Wilcox II, 2003).

Research on aerosol trends and sources of specific aerosols in Alaska show a decline in atmospheric aerosols in the Arctic since the 1980's (Polissar, 1998a; Polissar, 1998b; Wilcox, 2003). This research attributes this decline to emissions reductions in Europe and Russia. Emissions reductions in Europe, as well as in North America, are the results of improved environmental practices and green technology. In contrast, Russia's emissions decline was due to an economic change during the 1990's. However the forecast for Russian aerosol emissions is not as good. Russia's economic situation is vastly improving so its industrial output and therefore aerosol output are expected to increase.

To better understand the long-range transport of pollutants and their impact on the regional haze budget in Alaska, the Alaska Department of Environmental Conservation (ADEC) developed a short-term regional haze monitoring program. Because the Tuxedni, Simeonof, and Bering Sea Wilderness Areas are extremely remote and difficult to access, ADEC focused on DNPP. The goal for the monitoring study was two-fold:

1) To determine if either of the two existing IMPROVE sites adequately represents the entire park (DNPP covers 6 million acres)

and

2) To determine the contribution of long-range transport to regional haze in the park.

To achieve these two goals a larger aerosol sampling network was necessary. The Alaska Department of Environmental Conservation worked with the Geophysical Institute at the University of Alaska Fairbanks (UAF) to design and deploy an aerosol impactor sampling network around DNPP to characterize the aerosols entering the Park from each direction. Figure 2 shows the four aerosol impactor sampling sites used in the network: McGrath (west of DNPP), Lake Minchumina (northwest of DNPP), DNPP headquarters (eastern boundary of DNPP) and Trapper Creek (south of DNPP). The latter two sites were collocated with the two existing IMPROVE sites.

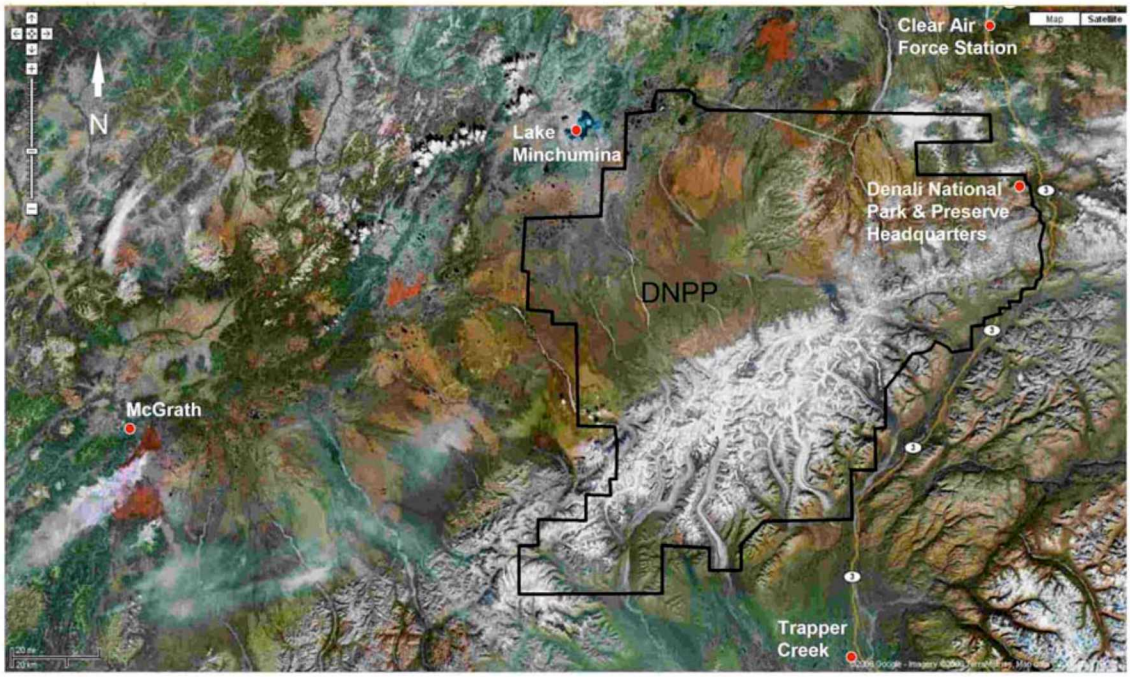

Figure 2. Satellite image showing the locations of the five planned monitoring sites (red dots). The black line represents the park boundary. Figure courtesy of ADEC.

The data obtained from the ADEC sampling network consists of aerosol concentrations for 28 selected elements between sodium and lead in three hour time steps from March 15, 2008 through June 30, 2009. These data are the basis for the analysis

presented in this thesis. These data were combined with other analysis methods to identify the sources and source regions for the observed aerosols. The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model system computed air parcel meteorological trajectories backward in time to help identify possible aerosol source regions (Draxler, 1997; Rolph, 2003; Draxler, 2003). Also, the Chemical Mass Balance (CMB) model, EPA-CMBv8.2 model (EPA, 2004), identified possible sources of the aerosols observed at a receptor (Cooper, 1980; Watson, 1984; Javitz, 1988a; Javitz, 1988b). After plotting the concentrations of the 28 different aerosol species, identifying specific aerosol component peaks, running HYSPLIT backward meteorological trajectories to determine source regions, and identifying potential sources using CMB, the results of the analyses were compared to determine the origins of the aerosols associated with observed peaks and quantify what fraction of the observed aerosol concentration is from local versus distant sources.

Chapter 2

Methodology

2.1 Sampling Sites

Four sampling sites were established around DNPP to sample air entering DNPP from any direction (Figure 2). These sites were located at: McGrath (west of DNPP), Lake Minchumina (northwest of DNPP), DNPP headquarters (eastern boundary of DNPP) and Trapper Creek (south of DNPP). The sites are described in the following sections.

2.1.1 McGrath

The McGrath site, established on February 6, 2008, was located near the National Weather Service office in McGrath (63.88278°N, -152.31222°W, 391 m Above Sea Level [ASL]). The region surrounding the site is shown in Figure 3.

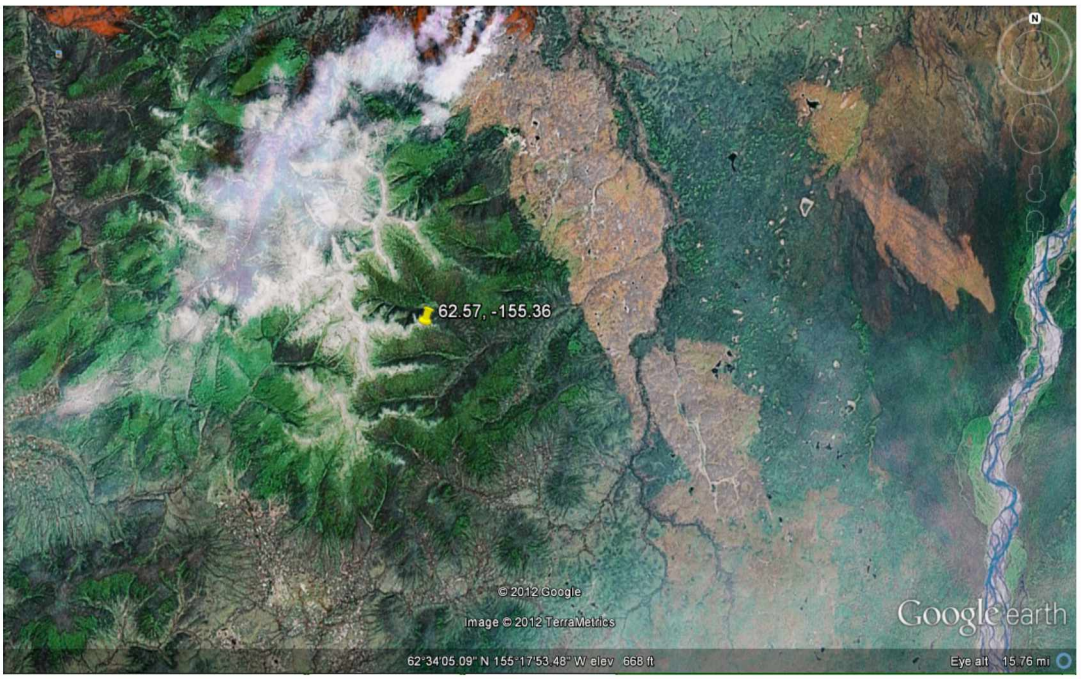

Figure 3. McGrath site. Figure from Google Earth.

2.1.2 Lake Minchumina

The Lake Minchumina site, established on February 7, 2008 although sampling did not start until February 24, 2008, was located in the community of Lake Minchumina (63.88278°N, -152.31222°W, 205 m ASL). The region surrounding the site is shown in Figure 4.

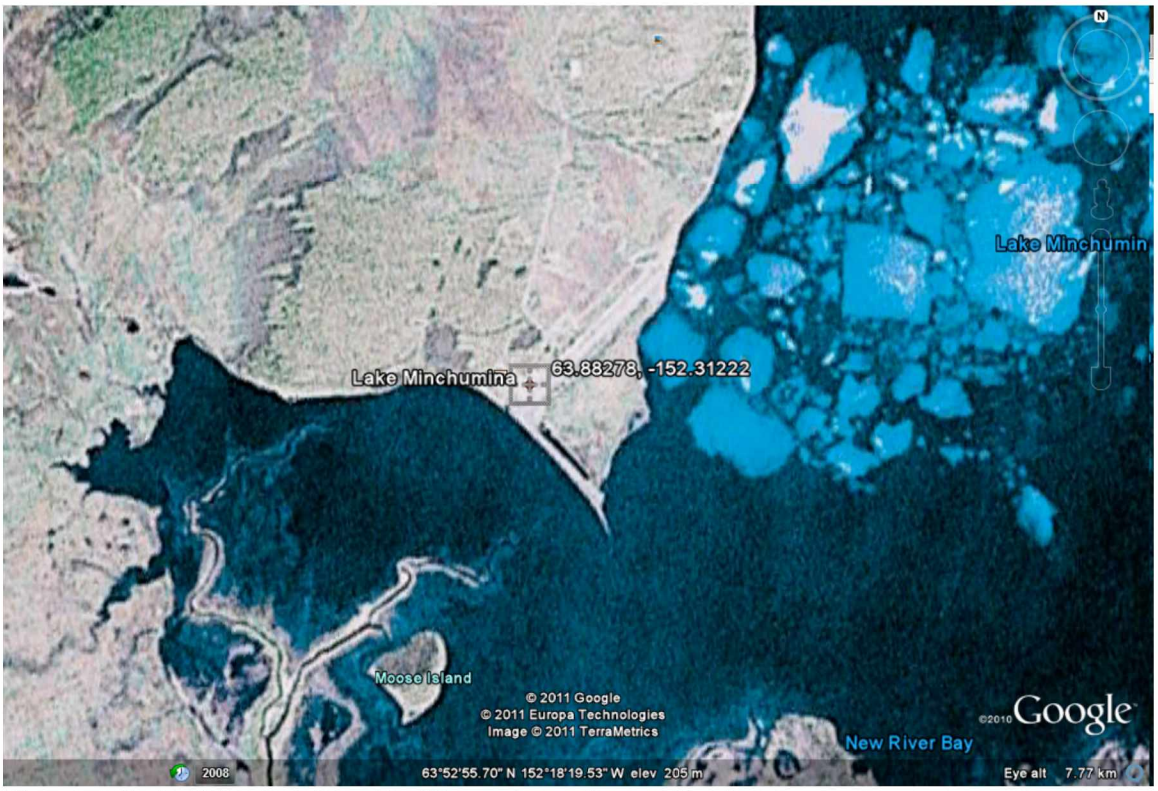

Figure 4. Lake Minchumina site. Figure from Google Earth.

2.1.3 DNPP Headquarters

The DNPP Headquarters site is located at Park Headquarters (63.7233°N, -148.9675°W, 660 m ASL). The DRUM sampler was installed on February 20, 2008, at the same site the IMPROVE sampler. The region surrounding the site is shown in Figure 5.

Figure 5. DNPP headquarters site. Figure from Google Earth.

2.1.4 Trapper Creek IMPROVE Site

The Trapper Creek site, established on February 19, 2008, is located near the Trapper Creek Elementary School (62.3153 °N, -150.3156 °W, 145 m ASL). The sampler was deployed at the same site as the IMPROVE sampler. The region surrounding the site is shown in Figure 6.

Figure 6. Trapper Creek site. Figure from Google Earth.

2.2 Davis Rotating Unit for Monitoring (DRUM)

The primary samplers used during this study were 3-stage DRUM aerosol impactors made by Integrity Manufacturing (Figures 7 and 8 and Cahill, 1985; Raabe, 1988). The 3-stage DRUM sampler is a cascade aerosol impactor that uses momentum to separate ambient aerosols into three size fractions 0.1-0.34, 0.34-1.15 and 1.15-2.5 microns (μm) in aerodynamic diameter as a function of time. The 2.5 micron size cut is set using a cyclone. Because DRUM samplers have been successfully used to collect size- and time-resolved aerosol elemental compositions and mass concentrations in remote regions around the world (Cahill, 1993; Wetzel, 2003; Collins, 2007) and they usually require limited human intervention to operate, these samplers appeared to be a

good choice for this experiment. However, the 11.5 liter per minute samplers, when left unattended for periods of time in harsh conditions, were unreliable and forced the investigators to switch to the more reliable 23 liters per minute samplers at Lake Minchumina and McGrath. Therefore, the flow rates of the samplers at DNPP and Trapper Creek were 11.5 liters per minute while the flow rates of the samplers at Lake Minchumina and McGrath were 23 liters per minute. Although the flow rates were different, the cut points for the samplers are identical.

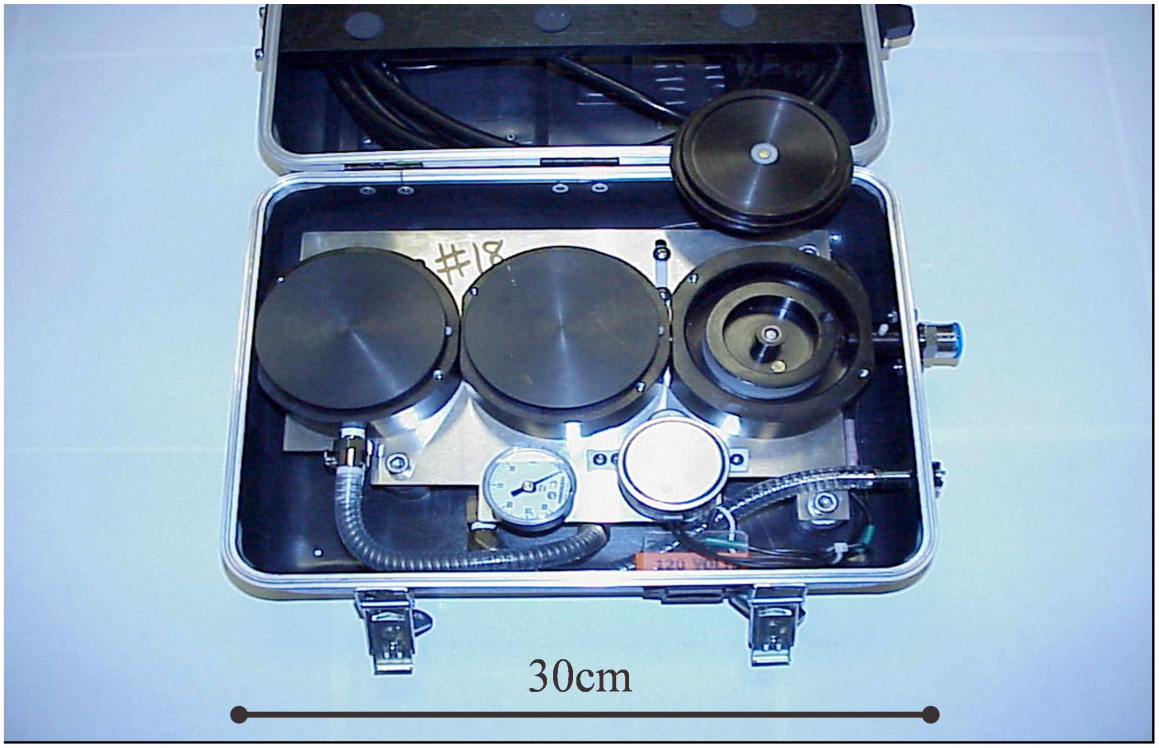

Figure 7. A 23 liters per minute DRUM sampler. Photo courtesy of T. Cahill (University of California, Davis).

Figure 8. A DRUM sampler at the Trapper Creek site. Photo courtesy of Breuninger (ADEC).

The DRUM impactors used in this study continuously collected aerosols on Apiezon-L™ coated Mylar™ strips. The Mylar™ strips were mounted on the metal sampling drums at UAF (Figure 9). The Mylar™ was then coated with a thin layer of Apiezon-L™ grease to prevent particle bounce. The samples were then placed in sample cups and sent to the field for installation in the DRUM sampler. Once the samples had been exposed for the desired duration, they were placed into sample cups and shipped back to UAF. Upon return to UAF the samples were removed from the metal drums and placed on labeled slide frames.

Figure 9. Aerosols collected on a Mylar™ strip wrapped around the metal cylinder described in the text. Photo courtesy of T. Cahill (University of California, Davis).

2.3 Aerosol Compositional Analyses

The aerosols on the Mylar™ strips were subjected to a variety of non-destructive analytical techniques including beta-gauge for aerosol mass (performed at UAF) and

synchrotron x-ray fluorescence (S-XRF) for elemental composition (performed at the Advanced Light Source at Lawrence Berkeley National Laboratory) with three hour time resolution. The S-XRF provides quantitative concentrations for 28 selected elements between sodium and lead (Cahill, 1999; Cahill, 2003). These methods follow the DRUM Quality Assurance Protocols (Available from the DELTA Group at the University of California, Davis). The quantitative elemental concentrations are determined from the S-XRF x-ray spectrum using NIST-traceable thin film standards that are analyzed multiple times during each analysis run. The analysis results in quantitative and reproducible elemental concentrations.

The raw data obtained from the mass and elemental analyses are multiplied by a conversion factor derived from the area of the sample analyzed on the Mylar^{TM} strip and the flow rate of the sampler. This factor turns the areal density for a specific element on the strip into an atmospheric concentration. The data from the strips are aligned, blank subtracted, and time stamped using information from the log sheet. The alignment, blanking, and time stamping produces the final data file for the period during which the strips were collected.

2.4 HYSPLIT Model

The National Oceanic and Atmospheric Administration's Air Resources Laboratory's HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) meteorological model is a system for computing air parcel trajectories forward or backward in time from a set starting location and time (Draxler, 1997; Rolph, 2003; Draxler, 2003). An example of a HYSPLIT model run output plot for the DNPP

headquarters site on May 28, 2009 is shown in figure 10. The resulting plots show a star at the point where the trajectory ends. Three lines converge on the star. Each line represents the backward trajectory for an air parcel that starts at a different height. The starting heights corresponding to each color are given on the graph below the plot. On each line there are a series of markers. The markers closest to the star represent where the air was 6 hours before the air parcel sampled at that site reached the star. The next marker is where the air parcel was 6 hours prior to that point and so on. The larger markers are where the air parcel was 24 hours prior to the star or previous large marker. By following the lines the areas the air parcel crossed during its transport to the site can be identified. The graph below the plot shows (going from the day the run starts on the left backwards in time to the right) the altitudes at which the air parcels moved during their transport to the site.

One HYSPLIT backward trajectory was computed every day of the DRUM sampling period (March 15, 2008 – June 30, 2009). The sites, as previously mentioned, are Trapper Creek (62.3153°N, -150.316°W, 145 m ASL), DNPP (63.7233°N, 148.9675°W, 660 m ASL), Lake Minchumina (63.88278°N, 152.312°W, 205 m ASL) and McGrath (62.95639°N, 155.596°W, 301 m ASL). The trajectories were modeled using the archived GDAS (Global, 2005 - Present) data (Kanamatsu, 1989). Each backward trajectory ran for 310 hours starting at 21 UTC. Each trajectory was run at six different heights (1500 meters above ground level [AGL], 2500 meters AGL, and 3500 meters AGL (low heights) 4500 meters AGL, 5500 meters AGL, and 6500 AGL) due to the fact that some of the aerosols transport in elevated layers. Vertical velocity was taken

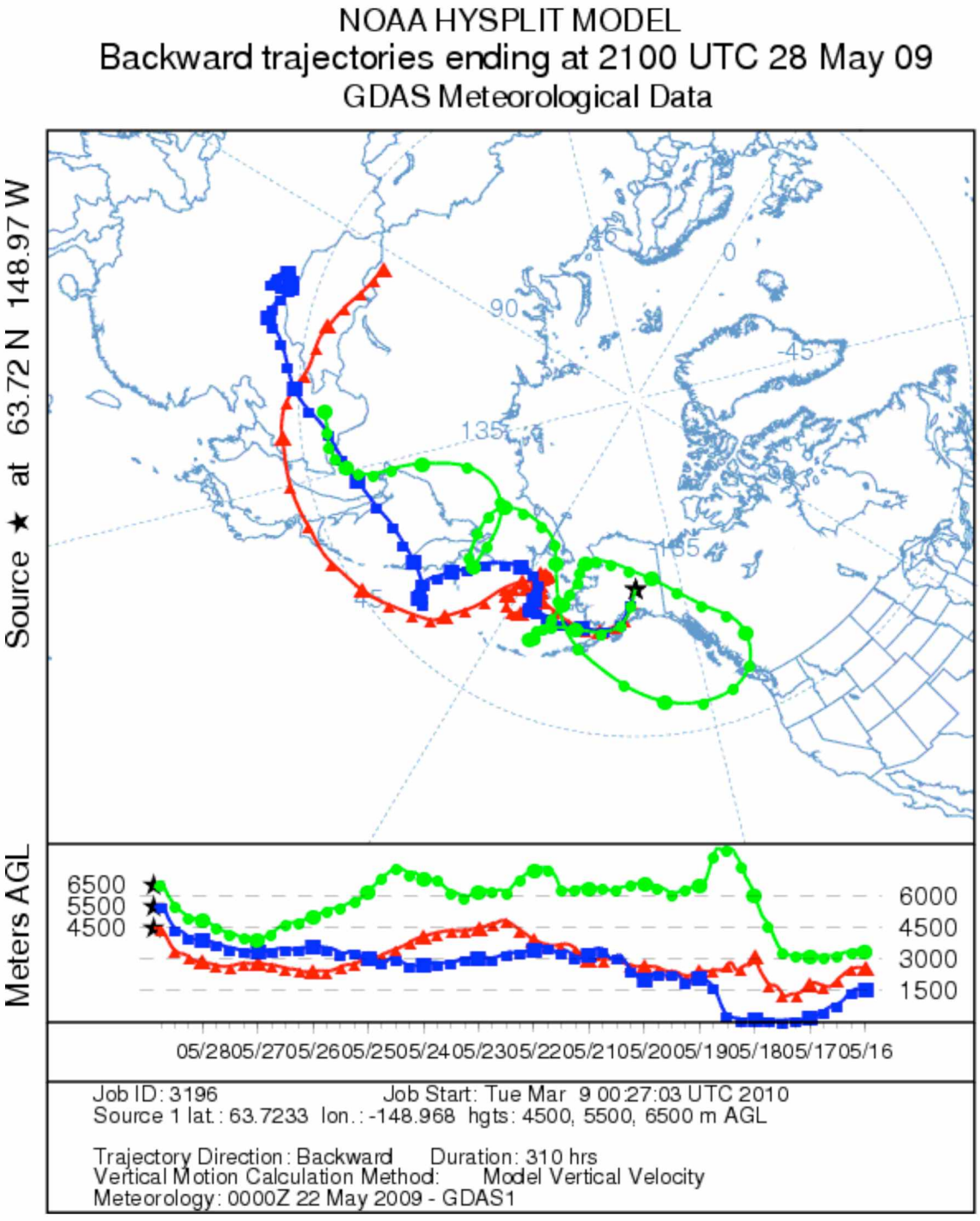

Figure 10. An example of a HYSPLIT model result for DNPP.

into account (Draxler, 1996). Each of the heights was simultaneously projected on a single polar map to show the transport of the air parcel.

After all of the HYSPLIT trajectories were computed they were individually analyzed to observe the path of the air parcel at each height. A chart was made to record where the air parcel traveled during transport. The chart specifically identified when the air parcel, no matter what height (either 4500, 5500, or 6500 meters AGL) traveled over possible source locations, such as the Taklimakan and Gobi deserts in China and Mongolia and Norilsk, Russia. To determine if the parcel passed over a certain area a circle or oval representing the approximate size of the location was drawn around the area. The Gobi Desert is approximately 1,500 km (932 mi) long (SE/NW) and has a width (N/S) of 800 km (497 mi) (Wikipedia 1, 2010), so an area of approximately 2,092 km (1300 mi) long (W/E) and 966 km (600 mi) wide (N/S) was used to represent the Gobi desert. The Taklamakan Desert is approximately 1,000 kilometers (620 mi) long and 400 kilometers (250 mi) wide (figure 11) (Wikipedia 2, 2010), so an area of approximately 660 mi long and 300 mi wide was used to represent the Taklamakan desert (figure 12). Norilsk is approximately 45 kilometers (20 mi) (figure 13), so an area with a radius of approximately 100 mi was used to represent Norilsk (figure 12).

Figure 11. A map of the Taklamakan and Gobi Deserts (Environmental Nature and Tourist Maps Enviro-Map.com).

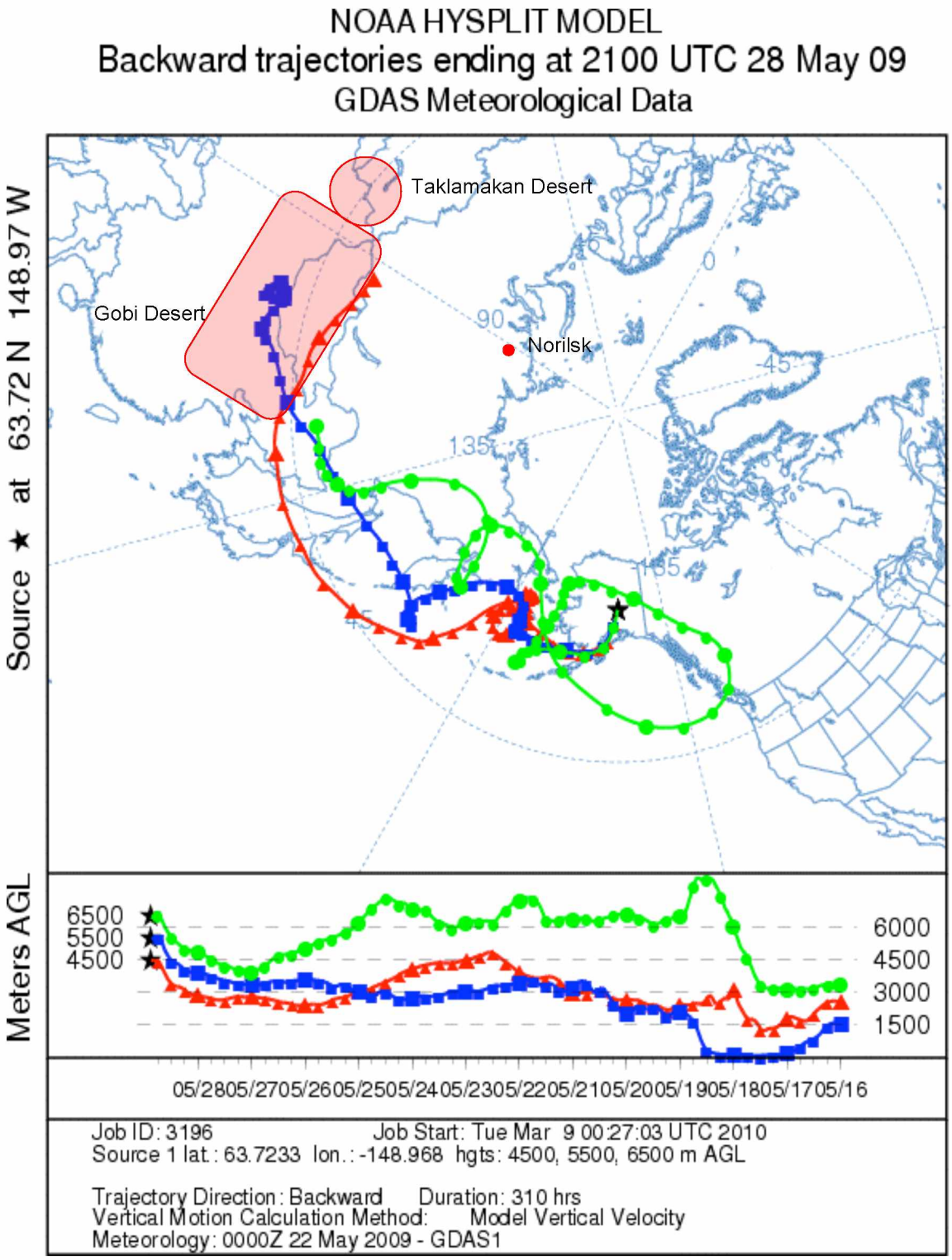

Figure 12. A HYSPLIT trajectory with the outlines of the areas used to identify if the trajectory has crossed a specific source region.

Figure 13. Map of Norilsk, Russia (Map of Russia.org).

If the air parcel trajectory crossed the area representing a specific location, that trajectory it received a 1; if it did not, it received a 2. An example of the chart is shown in table 1. These charts were made for each site for the entire study period.

Table 1. An example of a HYSPLIT chart for May 2009 at DNPP headquarters.

Date	Crossed Gobi	Crossed Taklamkan	Crossed Norilsk
5/1/2009	2	2	2
5/2/2009	2	2	2
5/3/2009	2	2	2
5/4/2009	1	1	2
5/5/2009	1	2	2
5/6/2009	2	2	1
5/7/2009	2	2	2
5/8/2009	2	2	2
5/9/2009	2	2	2
5/10/2009	1	1	2
5/11/2009	1	1	2
5/12/2009	1	2	1
5/13/2009	2	2	2
5/14/2009	2	2	2
5/15/2009	2	2	2
5/16/2009	2	2	2
5/17/2009	2	2	2
5/18/2009	1	1	2
5/19/2009	1	2	2
5/20/2009	1	2	2
5/21/2009	2	2	2
5/22/2009	1	2	2
5/23/2009	2	2	2
5/24/2009	2	2	2
5/25/2009	2	2	2
5/26/2009	1	2	2
5/27/2009	1	2	2
5/28/2009	1	2	2
5/29/2009	2	2	2
5/30/2009	2	2	2
5/31/2009	2	2	2

2.4 Chemical Mass Balance (CMB) Model

The Chemical Mass Balance (CMB) model, EPA-CMBv8.2 model (EPA, 2004), was run to confirm the source regions and discover the specific sources of the aerosols. The CMB model is one of several receptor models that have been applied in previous air quality studies (Stohl, 2007; Gatari, 2009). As stated in the EPA's peer review of the Chemical Mass Balance Model and Documentation booklet, "Receptor models use the chemical and physical characteristics of gases and particles measured in the exhaust of different sources and collected at a receptor site to both identify the presence of and to quantify the source contributions to receptor concentrations." (Schauer, 2005). CMB uses a linear least squares method to determine what mix of sources most closely resembles the aerosols observed at a receptor site (Cooper, 1980; Watson, 1984; Javitz, 1988a; Javitz, 1988b). The EPA's CMB model booklet also states that, "Receptor models are generally compared with dispersion models that use pollutant emissions rate estimates, meteorological transport, and chemical transformation mechanisms to estimate the contribution of each source to the receptor's concentrations. The two types of models are complementary, with each type having strengths that compensate for the weaknesses of the other." (Schauer, 2005).

Compound concentrations and uncertainties from the DRUM data set were used as receptor concentrations in the CMB along with a combination of two different sets of source profiles. The CMB results were optimized to obtain the best R^2 and maximum amount of explained mass.

The first set of source profiles was from the Northern Front Range Air Quality Study (NFRAQS) (Watson, 1998). This source profile set included information on each source composition including elements, ions, and organic and elemental carbon. Some of the source profiles included were vehicle emissions, wood burning, coal power plant emissions, and secondary particle formation profiles such as ammonium sulfate and ammonium nitrate.

The second set of source profiles was from the Portland Aerosol Characterization Study (PACS) (Watson, 1979). This set of profiles included sources that were similar to those in the NFRAQS set and some sources that were not included in the NFRAQS source profile set, such as marine aerosols, continental and urban dust, vegetative burn, and major types of furnaces.

These source profiles do not perfectly represent the aerosol emission sources found in the state of Alaska. However, there are no EPA-approved source profiles for the state of Alaska nor for any international sources, so the NFRAQS and the PACS profiles which do contain source profiles for sources that are commonly found in Alaska are the best source profiles available for running the CMB for Alaskan sites. For example in the NFRAQS and PACS profiles there are sources such as vegetative burn (like the wildfires that occur yearly in Alaska), marine aerosols (sea spray from the Pacific), and coal-fired power plants (representative of the Healy Power Plant near DNPP or Norilsk, Russia). These profiles were also used because they were generated for locations (PASC from Portland, Oregon and NFRAQS from Colorado) that are similar to Alaskan conditions such as with the weather and terrain. The mixed set of source profiles includes a mixture

of the NFRAQS and PACS profile sets (table 2). This set included all major sources (table 3) of the parameters that were being analyzed.

Table 2. The fitting species.

Parameter	DRUM	NFRAQS	PACS	Mix of NFRAQS and PACS
Aluminum	Yes	Yes	Yes	Yes
Ammonium Sulfate	Yes	No	No	No
Arsenic	Yes	Yes	No	No
Bromine	Yes	Yes	Yes	Yes
Calcium	Yes	Yes	Yes	Yes
Chlorine	Yes	Yes	Yes	Yes
Chromium	Yes	Yes	No	No
Cobalt	Yes	No	No	No
Copper	Yes	No	No	No
Gallium	Yes	No	No	No
Iron	Yes	Yes	Yes	Yes
Lead	Yes	Yes	Yes	Yes
Magnesium	Yes	Yes	Yes	Yes
Manganese	Yes	No	No	No
Molybdenum	Yes	No	No	No
Nickel	Yes	No	No	No
Phosphorus	Yes	Yes	No	No
Potassium	Yes	Yes	Yes	Yes
Potassium (Non-Soil)	Yes	No	No	No
Mass, $PM_{2.5}$ Reconstructed	Yes	No	No	No
Rubidium	Yes	Yes	No	No
Selenium	Yes	No	No	No
Silicon	Yes	Yes	Yes	Yes
Sodium	Yes	Yes	Yes	Yes
SOIL	Yes	No	No	No
Strontium	Yes	Yes	No	No

Table 2 Continued.

Sulfur	Yes	Yes	Yes	Yes
Titanium	Yes	No	No	No
Vanadium	Yes	No	No	No
Yttrium	Yes	No	No	No
Zinc	Yes	Yes	Yes	Yes
Zirconium	Yes	No	No	No

Table 3. A comparison of several source profiles in fraction of the profile due to each component. Note: The sum of these components will be less than one because the Regional Haze study did not collect all of the species in the profile so the species fit exclude those species not in both data sets.

Parameter	Marine aerosol	Coal-fired power plants	Continental dust	Vegetative burning
Aluminum	0	0.05968	0.117	0.0045
Arsenic	N/A	0	N/A	N/A
Bromine	0.002	0.000147	0	0.00045
Calcium	0.014	0.034536	0.0093	0.0092
Chlorine	0.4	0	0	0.099
Chromium	N/A	0.000176	N/A	N/A
Iron	0	0.02916	0.068	0.00054
Lead	0	0.00068	0.00006	0
Magnesium	0.048	0	0.0176	0
Phosphorus	N/A	0.009372	N/A	N/A
Potassium	0.014	0.004644	0.01	0.065
Rubidium	N/A	0.000053	N/A	N/A
Silicon	0	0.090112	0.254	0.0049
Sodium	0.4	0	0.0069	0.0033
Strontium	N/A	0.001964	N/A	N/A
Sulfate	0.1	0.101716	0	0.05
Sulfur	0.033	0.02948	0.0007	0.016
Zinc	0	0.000797	0.00041	0

For the CMB analysis two types of aerosols were examined, one represented soil (a.k.a. SOIL) and one represented industry. However, looking at the possible fitting

species there is neither a specific parameter unique to soil nor a specific parameter unique to industry. Therefore certain combinations of species were used to accurately represent SOIL and industry. The combinations were chosen based on previous research that looked at soil and industrial aerosols (Barrie, 1990; Li, 1990; Shaw, 1991; Air Resource Specialist, 1992; Polissar, 1998a; Polissar, 1998b; Okada, 2004; Pradhan, 2010). The parameters used by previous researchers to represent soil and industry are shown in tables 3 and 4 respectively. There is a commonality between the previous research for fitting species for soil and industry. Aluminum, silicon, calcium, and iron were used as soil signatures and zinc, sulfur, bromine, and lead were used as industrial emissions signatures. Chlorine and sodium were used as sea-spray signatures to identify the oceanic aerosols picked up during transport over the oceans surrounding Alaska. The CMB model was run for days identified as having high or low concentrations for the soil and industry-related species.

Table 4. Table of SOIL fitting species used in previous research.

Soil/dust composition (CMB fitting species)	Gobi Desert composition (Pradhan, 2010)	Taklamakan Desert composition (Okada, 2004)	Soil/dust composition (Air Resource Specialist, 1992)
Al	Al	Al	Al
Si	Si	Si	Si
Ca	Ca	Ca	Ca
Fe	Fe	Fe	Fe
	Ti	Ti	Ti
	Mg	K	
	Na	Mg	
	N	S	
Soil/Dust composition (Polissar 1998a, b)	**Soil/Dust composition (Shaw, 1991)**	**Soil/Dust composition (Barrie, 1990)**	**Soil/Dust composition (Li, 1990)**
Al	Al	Al	Al
Si	K	Si	Si
Ca	Fe	Fe	Ca
Fe	La	La	S
Ti	Sm	Sm	Cl
Mn	Cs	Th	
K		Sc	
Black Carbon			
S			
Cl			

Table 5. Table of industry fitting species used in previous research.

Industry composition (CMB fitting species)	Industry composition (Polissar, 1998a, b)	Industry composition (Shaw, 1991)	Industry composition (Barrie, 1990)	Industry composition (Li, 1990)
Zn	Zn	Zn	Zn	Zn
S	S	S	Ni	S
Br	Br	Br	V	Br
Pb	Cu	Cu	As	Si
	Pb	Ni	In	Cl
	Si	V	Mn	Trace Metals
	Black Carbon	As	Mo	
	H+	Black Carbon	Sb	
	Na	Mn	Se	
	SO_4	Se		
		SO_4		
		Heavy Metals		

Chapter 3

Results and Discussion

3.1 Aerosol Analysis

Aerosol composition and concentration data for the four DRUM monitoring sites was scheduled to be collected every three hours from March 15, 2008 through July 30, 2009 which would end with a total of 473 total days of data for each site. However, sampler failures, staffing shortages, and operator errors led to a number of missing periods. Table 6 shows the dates collected for each site during the study period. The sites at DNPP HQ and Lake Minchumina had the best data recovery rates (table 7).

The data from the DRUM samplers, as described in Section 2, included aerosol concentration measurements for 28 selected elements between sodium and lead. From this elemental concentration data, four additional quantities (NHSO, SOIL, KNON, and RCON as described below) were derived following Malm (1994) and included in the analysis. All of these elements/derived quantities, hereafter referred to as parameters, are shown in table 8. The assumptions used in the derivation of these quantities' can be found at: http://vista.cira.colostate.edu/improve/Publications/SOPs/UCDavis_SOPs/sop351.pdf

NHSO is a derived quantity representing ammonium sulfate. If all of the sulfur collected on the sample is assumed to be in the form of ammonium sulfate, the sulfur concentration obtained from S-XRF is multiplied by 4.125 to account for the nitrogen, hydrogen and oxygen atoms attached to each sulfur atom and results in the derived parameter NHSO (Malm, 1994). This assumption is reasonable for aged sulfur-containing aerosols if there is enough ammonium available in the atmosphere to

neutralize the sulfuric acid produced by the reaction of water and sulfur dioxide gas (Air Resource Specialists, 1992; Malm, 1994; Seinfeld, 2006).

Table 6. Dates of collection of collocated DRUM samplers. Recorded start and stop times are shown in brackets.

McGrath	
Date/Time On	05/28/2008 [16:00]
Date/Time Off	07/05/2008 [04:00]
Date/Time On	08/13/2008 [07:45]
Date/Time Off	09/22/2008 [10:45]
Date/Time On	09/25/2008 [10:25]
Date/Time Off	11/07/2008 [01:25]
Date/Time On	02/06/2009 [14:00]
Date/Time Off	03/04/2009 [08:00]
Lake Minchumina	
Date/Time On	02/24/2008 [11:25]
Date/Time Off	03/26/2008 [08:25]
Date/Time On	06/18/2008 [11:00]
Date/Time Off	07/29/2008 [11:00]
Date/Time On	08/07/2008 [11:53]
Date/Time Off	09/17/2008 [23:53]
Date/Time On	09/29/2008 [10:00]
Date/Time Off	11/11/2008 [10:00]
Date/Time On	11/20/2008 [11:20]
Date/Time Off	12/31/2008 [17:20]
Date/Time On	01/31/2009 [12:00]
Date/Time Off	03/13/2009 [21:00]
Denali Headquarters	
Date/Time On	02/26/2008 [16:00]
Date/Time Off	03/25/2008 [16:00]
Date/Time On	03/25/2008 [17:00]
Date/Time Off	05/07/2008 [02:00]
Date/Time On	05/07/2008 [11:12]
Date/Time Off	06/17/2008 [23:12]
Date/Time On	08/06/2008 [12:31]
Date/Time Off	09/17/2008 [00:31]
Date/Time On	09/17/2008 [12:20]
Date/Time Off	10/30/2008 [00:20]
Date/Time On	12/29/2008 [16:23]
Date/Time Off	02/02/2009 [13:23]
Date/Time On	02/02/2009 [16:26]
Date/Time Off	03/17/2009 [07:26]

Table 6. Continued.

Date/Time On Date/Time Off	04/30/2009 [15:33] 06/11/2009 [03:30]
Date/Time On Date/Time Off	06/11/2009 [20:30] 06/30/2009 [23:30]
Trapper Creek	
Date/Time On Date/Time Off	08/12/2008 [12:30] 09/21/2008 [09:30]
Date/Time On Date/Time Off	10/07/2008 [12:30] 11/04/2008 [15:30]
Date/Time On Date/Time Off	05/06/2009 [12:30] 06/02/2009 [12:30]
Date/Time On Date/Time Off	06/02/2009 [15:30] 06/25/2009 [15:30]

Table 7. Number of monitored days at each site at DNPP.

Site	# of Monitored Days
McGrath	151
Lake Minchumina	224
DHQ	323
Trapper Creek	121

SOIL is a derived quantity representing the mass concentration associated with the elements commonly associated with the earth's crust (Al, Si, Ca, K, Fe, and Ti) and their oxides (Barrie, 1990; Li, 1990; Shaw, 1991; Air Resource Specialist, 1992; Malm, 1994; Polissar, 1998a; Polissar, 1998b; Okada, 2004; Pradhan, 2010). The constants used to account for the masses of all of the elements attached to a crustal element due to its common oxides (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, and TiO_2) were empirically determined for soils from the western U.S. For example, iron is assumed to be evenly distributed between FeO and Fe_2O_3 so the iron concentration is multiplied by 1.36, the average of the factors (1.29 and 1.43, respectively) that the iron concentration must be multiplied by to account for the oxygen atoms attached to the iron atoms in these states.

All of the well-accepted crustal elements are handled this way so the resulting equation is:

$$SOIL = 2.20*Al + 3.48*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti$$

where Al, Si, Ca, Fe, and Ti are the concentrations of those elements obtained from S-XRF.

Table 8. List of parameter details.

Parameter	Abbreviation	Measured or Calculated	Analytical Techniques or Equation
Aluminum	Al	Measured	Gravimetric, S-XRF
Ammonium Sulfate	NHSO	Calculated	4.125 * S
Arsenic	As	Measured	Gravimetric, S-XRF
Bromine	Br	Measured	Gravimetric, S-XRF
Calcium	Ca	Measured	Gravimetric, S-XRF
Chlorine	Cl	Measured	Gravimetric, S-XRF
Chromium	Cr	Measured	Gravimetric, S-XRF
Cobalt	Co	Measured	Gravimetric, S-XRF
Copper	Cu	Measured	Gravimetric, S-XRF
Gallium	Ga	Measured	Gravimetric, S-XRF
Iron	Fe	Measured	Gravimetric, S-XRF
Lead	Pb	Measured	Gravimetric, S-XRF
Magnesium	Mg	Measured	Gravimetric, S-XRF
Manganese	Mn	Measured	Gravimetric, S-XRF
Mass, $PM_{2.5}$ Reconstructed	RCON	Calculated	NHSO + SOIL + (1.4 * KNON) + (2.5 * Na)
Molybdenum	Mo	Measured	Gravimetric, S-XRF
Nickel	Ni	Measured	Gravimetric, S-XRF
Phosphorus	P	Measured	Gravimetric, S-XRF
Potassium	K	Measured	Gravimetric, S-XRF
Potassium (Non-Soil)	KNON	Calculated	K – (0.60 * Fe)
Rubidium	Rb	Measured	Gravimetric, S-XRF
Selenium	Se	Measured	Gravimetric, S-XRF
Silicon	Si	Measured	Gravimetric, S-XRF n
Sodium	Na	Measured	Gravimetric, S-XRF

Table 8. Continued.

Parameter	Abbreviation	Measured or Calculated	Analytical Techniques or Equation
Soil	SOIL	Calculated	2.20 * Al + 3.48 * Si + 1.63 * Ca + 2.42 * Fe + 1.94 * Ti
Strontium	Sr	Measured	Gravimetric, S-XRF
Sulfur	S	Measured	Gravimetric, S-XRF
Titanium	Ti	Measured	Gravimetric, S-XRF
Vanadium	V	Measured	Gravimetric, S-XRF
Yttrium	Y	Measured	Gravimetric, S-XRF
Zinc	Zn	Measured	Gravimetric, S-XRF
Zirconium	Zr	Measured	Gravimetric, S-XRF

Potassium comes from both soil and biomass burning. It cannot be separated into these categories through the S-XRF analysis used to obtain these elemental concentrations, so other elements are used to separate the sources of the potassium. The amount of potassium in soil is represented by the ratio of potassium to iron in 'average' western soils, 0.6 (Malm et al., 1994). Therefore, KNON, the amount of potassium not associated with soil is the potassium concentration minus 0.6 multiplied by the concentration of iron:

KNON = potassium concentration – 0.6*Fe

The summation of all of the concentrations obtained from these additional variable equations, plus a sodium factor that represents sea salt, provides the 'reconstructed mass'.

RCON = NHSO + SOIL + 1.4KNON + 2.5*Na

The reconstructed mass is the aerosol mass concentration due to sulfur in the form of ammonium sulfate, soil elements and their oxides, potassium from biomass burning and sea salt. These are the main inorganic contributors to aerosol mass concentrations and the only portions of the mass concentration obtainable from S-XRF.

Graphs of the parameter concentrations were made for each sampling period. An example is shown in figure 14. They also show the variability of the measured and derived parameters. Figure 14 shows how well the elemental components of 'SOIL' track each other.

To determine where the aerosols affecting visibility in Denali National Park and Preserve are coming from the periods with the highest aerosol concentrations and the

most visibility degradation due to aerosols were investigated and compared to the periods with the lowest concentrations. To achieve this goal, the times and dates of high aerosol concentrations, also known as an aerosol event, had to be established. An event occurs when a parameter's concentration is twice the average for the parameter during the specified time frame, in this case

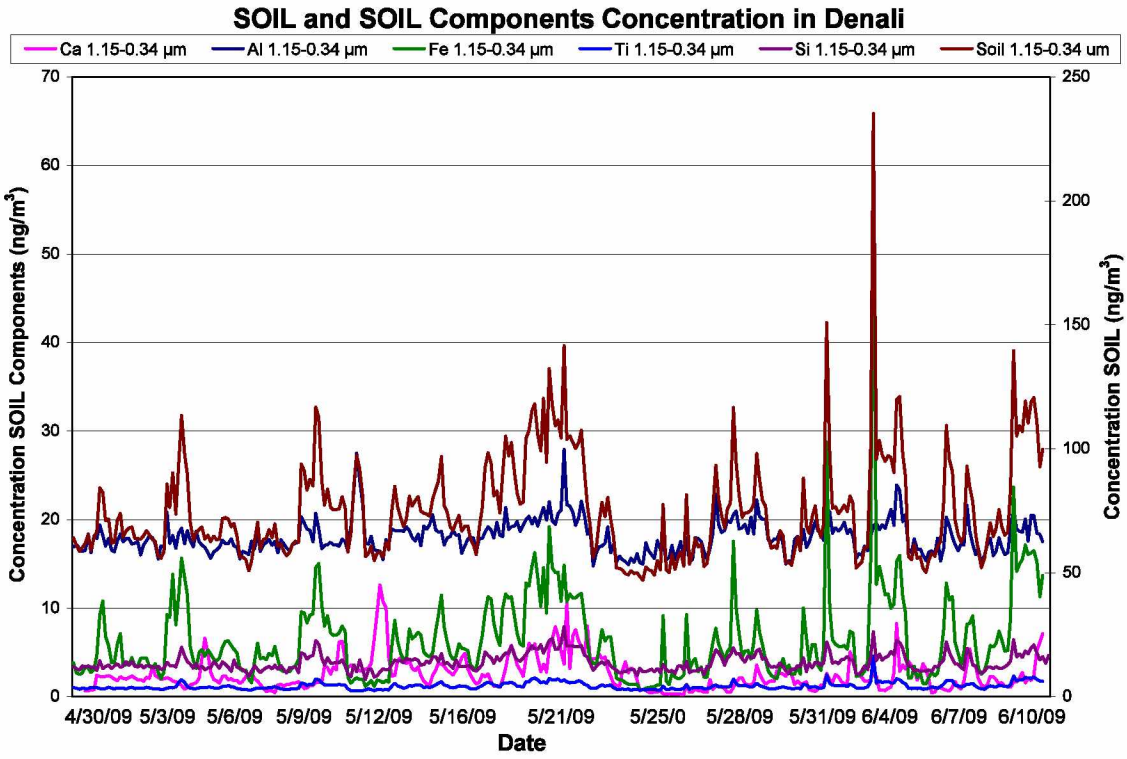

Figure 14. An example graph of the potassium concentrations as a function of time and size fraction. A similar graph was compiled for every species analyzed.

the season. There are four seasons: spring (March, April, May), summer (June, July, August), fall (September, October, November), and winter (December, January, February). The value corresponding to twice the average concentration of the parameter is defined as the event threshold.

The average, event threshold, minimum, maximum, and standard deviation for the concentration of each parameter for each size fraction were calculated. An example of a parameters average, event threshold, minimum, maximum, and standard deviation is shown in table 9. Once the event threshold was calculated for each species for each season and size fraction, the concentration values for each parameter could be sorted into dates that were associated with events and dates that were not associated with events. An example of this is shown in table 10.

Table 9. Potassium as a function of size at the Denali Headquarters site for Spring 2009.

Stat/Size Fraction (µm)	$PM_{2.5}$	2.50 – 1.15 µm	1.15 – 0.34 µm	0.34 – 0.10 µm
Average Concentration	6.6 ± 0.4 µm	3.6 ± 0.3 µm	2.4 ± 0.2 µm	0.6 ± 0.1 µm
Event Threshold	13.3 ± 0.9 µm	7.1 ± 0.5 µm	4.8 ± 0.4 µm	1.3 ± 0.1 µm
Maximum Concentration	21.8 ± 1. 6 µm	14.0 ± 1.0 µm	6.7 ± 0.5 µm	2.4 ± 0.2 µm
Minimum Concentration	0.4 ± 0.0 µm	0.0 ± 0.0 µm	0.0 ± 0.0 µm	0.0 ± 0.0 µm
Standard Deviation	3.6 ± 0.2 µm	2.4 ± 0.2 µm	1.3 ± 0.1 µm	0.5 ± 0.0 µm

Table 10. Potassium (size $PM_{2.5}$) data for Spring 2009 sorted into event categories at DHQ.

Total # of periods	382
Event	
# of times	18
Percent of total	5%
No Event	
# of times	364
Percent of total	95%

These data show that certain seasons have more events than others. Looking at 'SOIL' events (in all size fractions) there is an increase in the percentage of events during the winter and spring seasons compared to summer and fall seasons. However the

increase in percentage is not always consistent between the four sampling sites. The lack of consistency is due to a couple of reasons. The first being lack of collected data at certain sites which affects the statistics calculation. The lack of data makes the statistics very low/high when there is a small amount of data. However when there is sufficient amount of data there is not always agreement. The lack of consistency could also be due to weather patterns, landscape, and local influence. But more often than not, there is agreement between sites.

The reconstructed masses measured at DHQ, Trapper Creek, Lake Minchumina, and McGrath are given as functions of particle size in table 11 and figure 15. These results

Table 11. Reconstructed mass concentration as a function of size at DHQ, Lake Minchumina, Trapper Creek and McGrath. The standard deviations are given in the line below each average. The errors stated are the propagated analytical errors.

Calculated Statistic	DHQ	Trapper Creek	Lake Minchumina	McGrath
Average $PM_{2.5}$ RCON (ng m^{-3})	876.1 ±101.2	806.4 ±34.4	304.0 ±12.6	687.1 ±24.9
Standard deviation of $PM_{2.5}$ RCON (ng m^{-3})	927.1 ±206.0	1067.3 ±76.0	310.7 ±13.2	789.8 ±33.5
Average 2.5-1.15 µm RCON (ng m^{-3})	268.3 ±11.8	219.4 ±10.5	57.9 ±2.7	232.6 ±10.5
Standard deviation of 2.5-1.15 µm RCON (ng m^{-3})	295.8 ±13.3	386.1 ±21.1	89.4 ±4.7	388.2 ±20.9
Average 1.15-0.34 µm RCON (ng m^{-3})	438.2 ±28.5	434.5 ±27.3	182.4 ±10.8	285.1 ±16.4
Standard deviation of 1.15-0.34 µm RCON (ng m^{-3})	925.1 ±105.4	814.6 ±73.5	189.4 ±11.8	392.8 ±24.6
Average 0.34-0.1 µm RCON (ng m^{-3})	161.1 ±10.9	152.6 ±9.3	63.7 ±3.9	169.4 ±10.3
Standard deviation of 0.34-0.1 µm RCON (ng m^{-3})	256.3 ±17.4	193.7 ±12.3	87.4 ±5.6	240.3 ±14.8

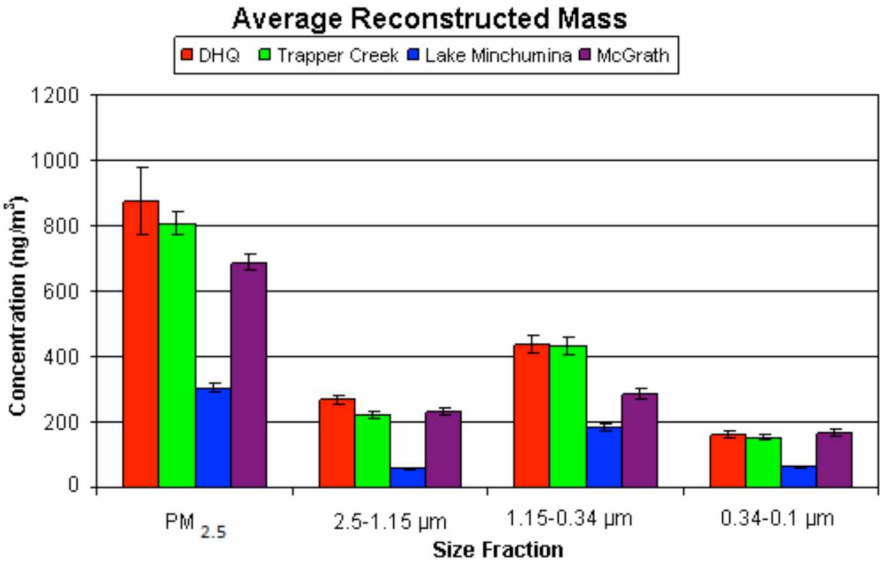

Figure 15. A bar chart showing average reconstructed mass concentrations as a function of size and site.

show that on average, DHQ and Trapper Creek have about the same concentrations of reconstructed mass.

The McGrath measurements are slightly lower in concentration due to a smaller concentration of particles in the 1.15-0.34 mm size fraction. Lake Minchumina is much lower in overall aerosol concentration possibly due to its location as the last of the sites to be impacted by transport coming up from the southwest. The variability of these values is shown by the standard deviations.

The concentration of the mass that is due to ammonium sulfate (NHSO) is again statistically the same at DHQ and Trapper Creek, with McGrath being slightly lower (table 12 and figure 16). The ammonium sulfate is the largest contributor to the reconstructed mass at all three of the previously mentioned sites during the winter and spring seasons while it has a smaller contribution during the Summer and Fall. In addition, all three sites show the highest concentrations of ammonium sulfate in the 1.15-

0.34 µm size fraction, the accumulation mode, which is consistent with the ammonium sulfate being due to aged emissions.

Table 12. Ammonium sulfate concentration as a function of size at DHQ, Trapper Creek, Lake Minchumina, and McGrath.

	DHQ	Trapper Creek	Lake Minchumina	McGrath
Average $PM_{2.5}$ NHSO (ng m^{-3})	615.9 ±33.4	565.8 ±30.5	213.3 ±11.6	407.7 ±20.2
Standard deviation of $PM_{2.5}$ NHSO (ng m^{-3})	1028.4 ±105.4	900.2 ±75.1	236.8 ±12.6	516.8 ±28.6
Average 2.5-1.15 µm NHSO (ng m^{-3})	97.5 ±6.9	114.0 ±8.0	14.0 ±1.0	54.9 ±3.9
Standard deviation of 2.5-1.15 µm NHSO (ng m^{-3})	123.4 ±8.7	284.3 ±20.0	21.3 ±1.5	107.8 ±7.8
Average 1.15-0.34 µm NHSO (ng m^{-3})	370.4 ±28.0	330.4 ±24.5	147.2 ±10.3	217.2 ±15.4
Standard deviation of 1.15-0.34 µm NHSO (ng m^{-3})	829.9 ±104.3	713.8 ±72.6	167.9 ±11.8	338.0 ±24.5
Average 0.34-0.1 µm NHSO (ng m^{-3})	139.7 ±9.9	121.4 ±8.6	52.1 ±3.7	135.6 ±9.6
Standard deviation of 0.34-0.1 µm NHSO (ng m^{-3})	235.3 ±17.5	173.3 ±12.2	78.7 ±5.6	208.8 ±14.9

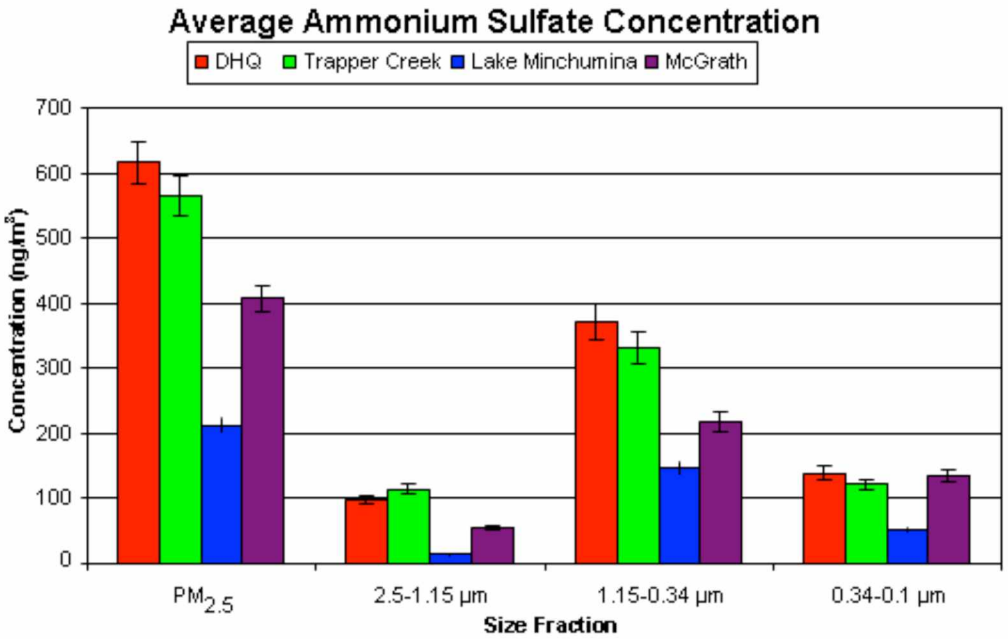

Figure 16. A bar chart showing average ammonium sulfate concentrations as a function of size and site.

Soil component concentrations (SOIL) showed uniformity across the three sites for the $PM_{2.5}$ concentration (table 13 and figure 17). However, unlike the ammonium sulfate, SOIL showed different behavior at the three sites. DNPP and McGrath showed a decrease in soil concentration as the size fraction decreased. A decrease in soil concentration as the size fraction decreases is expected as crustal components tend to be mechanically generated and larger in size than anthropogenically-produced aerosols so we observe a small tail in crustal component concentrations that decreases as the size of the particle size decreases (Seinfeld, 2006). Trapper Creek, in contrast, shows approximately the same concentrations in the two largest size fractions. All three sites show approximately the same concentration in the smallest size fraction.

The monthly average ammonium sulfate and SOIL concentrations at DHQ are shown in figures 18 and 19. A striking difference in both plots is the variability between years as shown by the differences between April through June, 2008, and April through June, 2009. For example, the concentration of ammonium sulfate in April 2008 is approximately 9 times larger than the concentration of ammonium sulfate in April 2009. Another example is that the concentration of SOIL in June 2009 is approximately 6 times that in June 2008. This variability implies that different transport or emission scenarios can greatly impact the concentration of an aerosol species at a site. Ammonium sulfate is a tracer of pollution and SOIL is a tracer of dust. One can see that there is seasonality in both records. The ammonium sulfate and the SOIL concentrations peak during the spring season. That correlates with the seasonality of Arctic Haze and Asian Dust events.

Table 13. SOIL as a function of size at DHQ, Trapper Creek, Lake Minchumina, and McGrath.

	DNPP	Trapper Creek	Lake Minchumina	McGrath
Average $PM_{2.5}$ SOIL (ng m^{-3})	227.4 ±8.3	229.9 ±10.0	60.8 ±2.2	213.7 ±7.0
Standard deviation of $PM_{2.5}$ SOIL (ng m^{-3})	295.6 ±14.6	256.5 ±16.6	75.1 ±2.8	304.7 ±9.6
Average 2.5-1.15 µm SOIL (ng m^{-3})	144.4 ±6.6	98.9 ±4.8	22.7 ±1.2	128.2 ±5.7
Standard deviation of 2.5-1.15 µm SOIL (ng m^{-3})	189.8 ±8.7	144.3 ±7.5	44.1 ±2.3	209.5 ±9.1
Average 1.15-0.34 µm SOIL (ng m^{-3})	63.4 ±3.4	101.8 ±6.4	28.2 ±1.5	53.9 ±2.6
Standard deviation of 1.15-0.34 µm SOIL (ng m^{-3})	116.0 ±12.1	170.8 ±15.6	34.7 ±1.6	76.7 ±3.4
Average 0.34-0.1 µm SOIL (ng m^{-3})	19.3 ±1.1	29.3 ±2.0	9.9 ±0.6	31.6 ±1.6
Standard deviation of 0.34-0.1 µm SOIL (ng m^{-3})	25.9 ±1.5	48.1 ±2.9	18.3 ±1.1	49.0 ±2.3

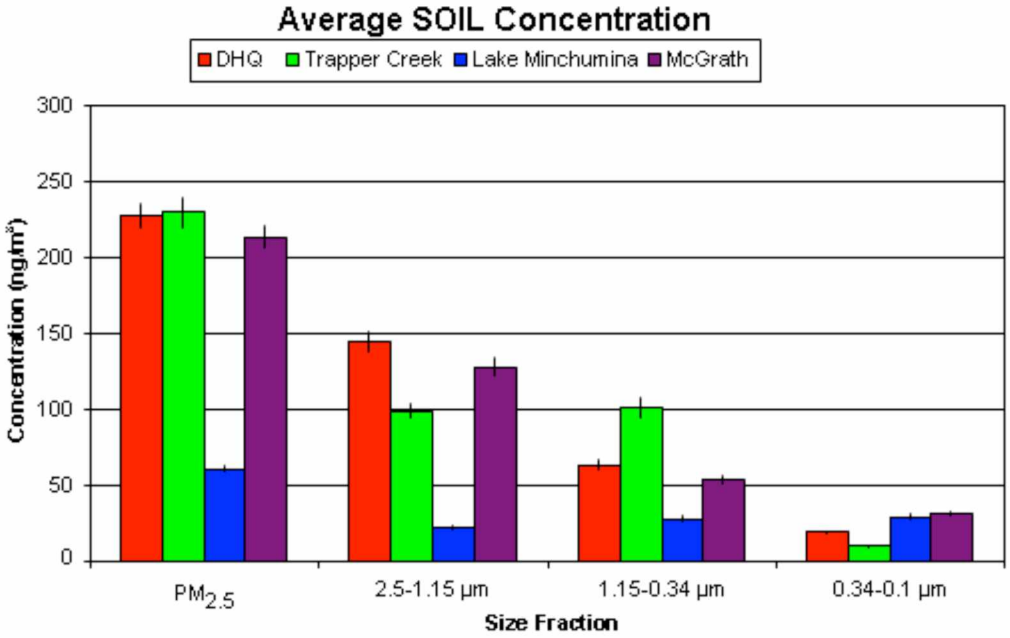

Figure 17. A bar chart showing average SOIL concentrations as a function of size and site.

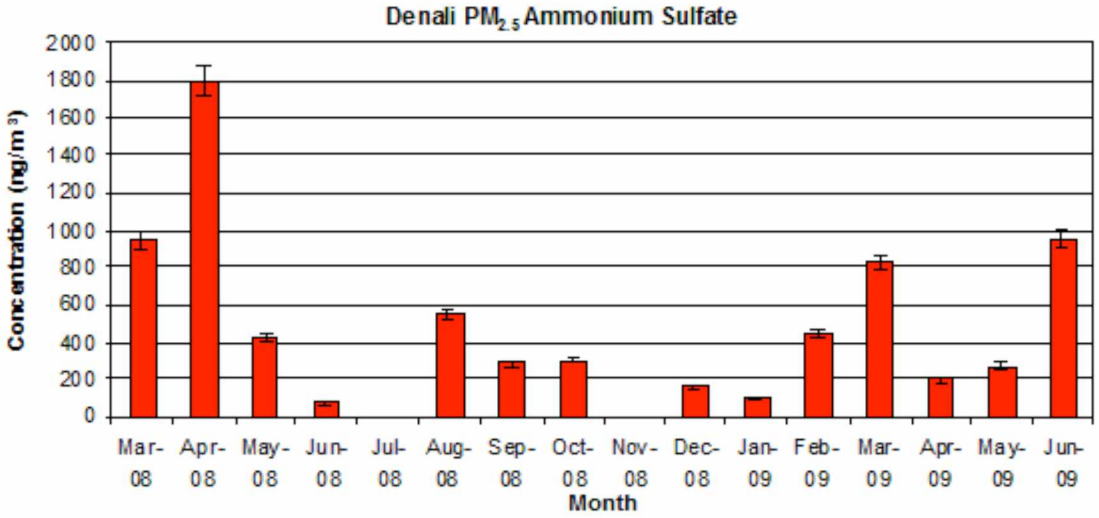

Figure 18. A bar chart showing $PM_{2.5}$ ammonium sulfate averages as a function of month at DHQ. The months with no bars show where data is missing.

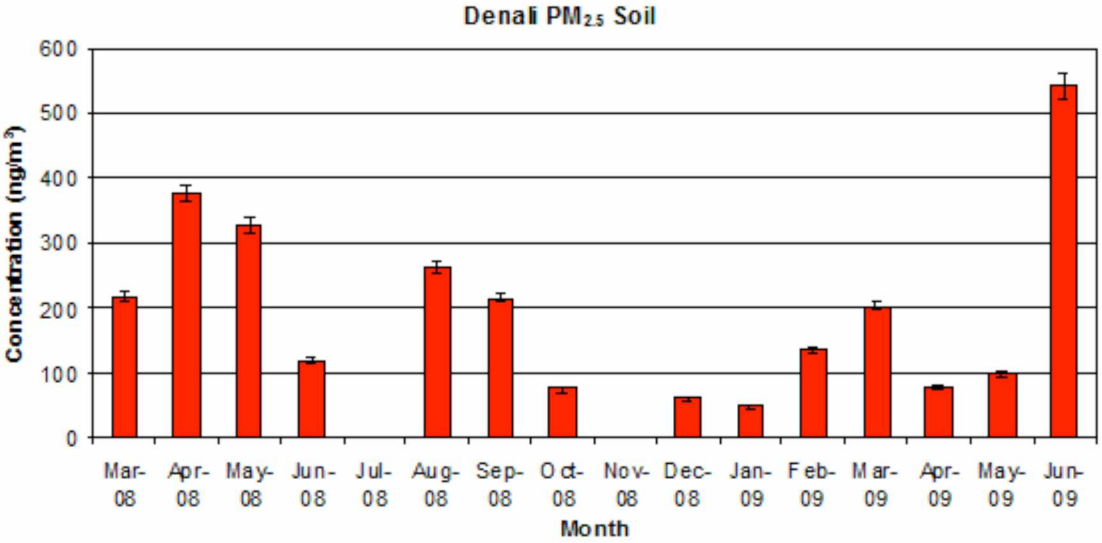

Figure 19. A bar chart showing $PM_{2.5}$ SOIL averages as a function of month at DHQ. The months with no bars show where data is missing.

Potassium (K) has two major sources, soil and smoke. Soil potassium will be on coarse particles, and smoke potassium, called KNON, will be found on much smaller particles. The soil potassium is estimated from the measured concentration of iron (Fe) and the ratio of potassium to iron, which should be about 0.6. If the ratio were slightly

smaller than 0.6, the KNON values will be negative, and there is no smoke. Therefore any residual potassium is assumed to be produced by smoke. The calculation, then of KNON, is the total potassium minus the calculated potassium from soil, or K- 0.6*[Fe].

Figure 20 shows the average concentration of KNON at DHQ for the entire sampling period. This graph shows smoke is present year round but the majority of it is during the late spring and summer months. The smoke is due to the wildfire season in Alaska. However the patterns of the seasonality are very similar to the other three sites.

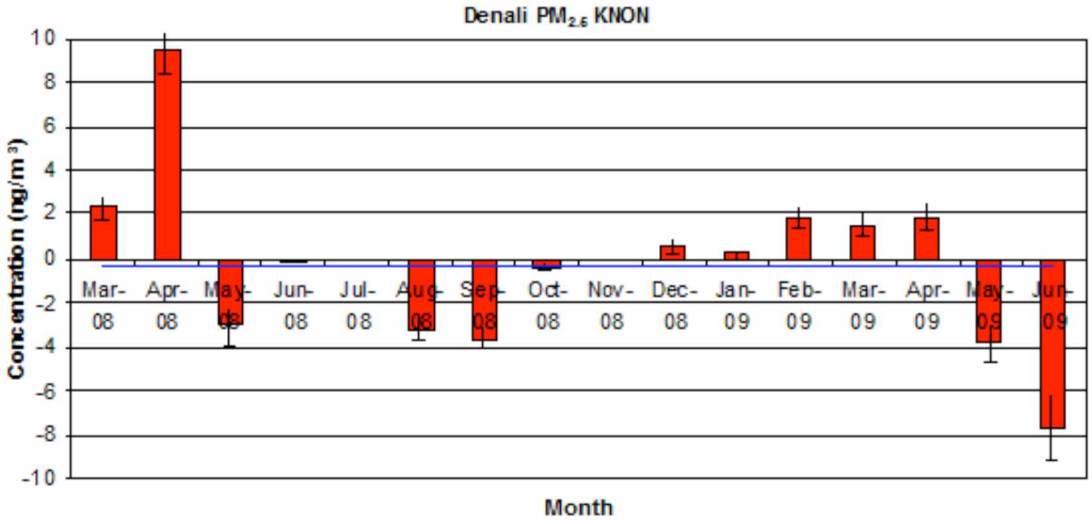

Figure 20. A bar chart showing $PM_{2.5}$ Non-Soil Potassium (KNON) averages as a function of month at DHQ. The months with no bars show where data is missing.

3.2 HYSPLIT Analysis Results

The HYSPLIT trajectories were analyzed to determine if an air parcel crossed a specified source region on its way to one of the study sites. Figures 21-24 show the percentage of time that an air parcel crossed one of the three source locations (Gobi Desert, Taklamakan Desert, and Norilsk, Russia) on its way to a selected site. The percentage of time that an air parcel crossed either the Gobi Desert, Taklamakan Desert, or Norilsk, Russia on its way to a selected site is much less than the percentage of time

when the trajectories did not cross the source regions on the way to the site. The percentage of time trajectories did not cross a source region versus the percent of time it crossed at least one of the source regions at each site were also calculated (figure 25). This calculation counts the Gobi Desert and the Taklamakan as one source region because about half of the time (46% at McGrath, 63% at Lake Minchumina, 63% at DHQ, and 41% at Trapper Creek) the trajectory crossed the Gobi it also crossed the Taklamakan.

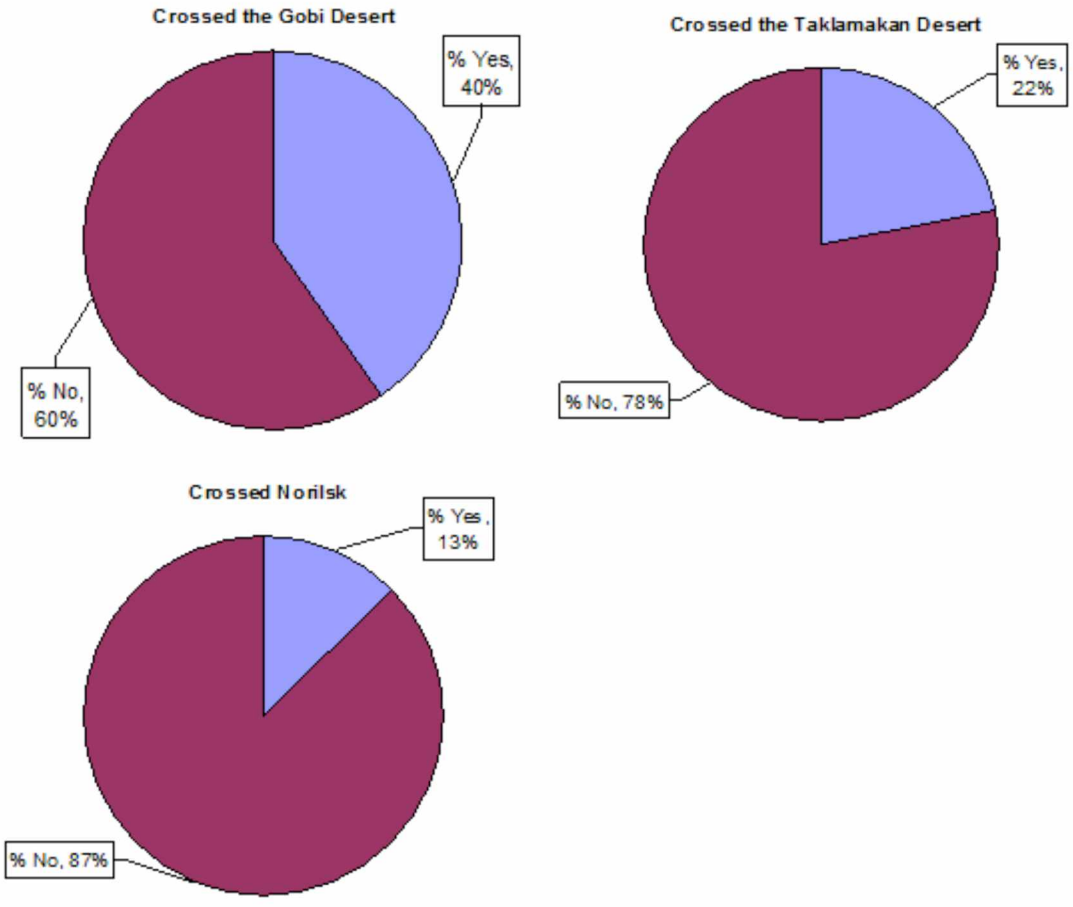

Figure 21. The percentage of time that DHQ trajectories crossed a certain source region during transport.

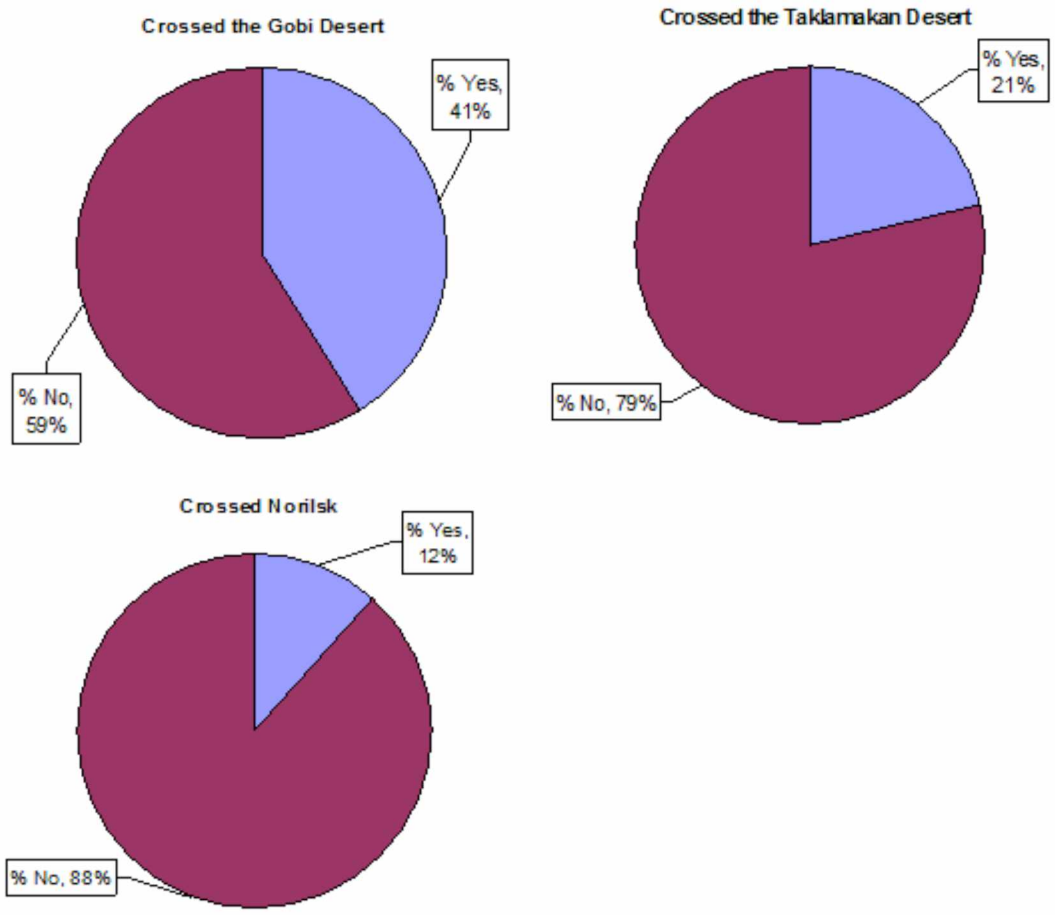

Figure 22. The percentage of time that Lake Minchumina trajectories crossed a certain source region during transport.

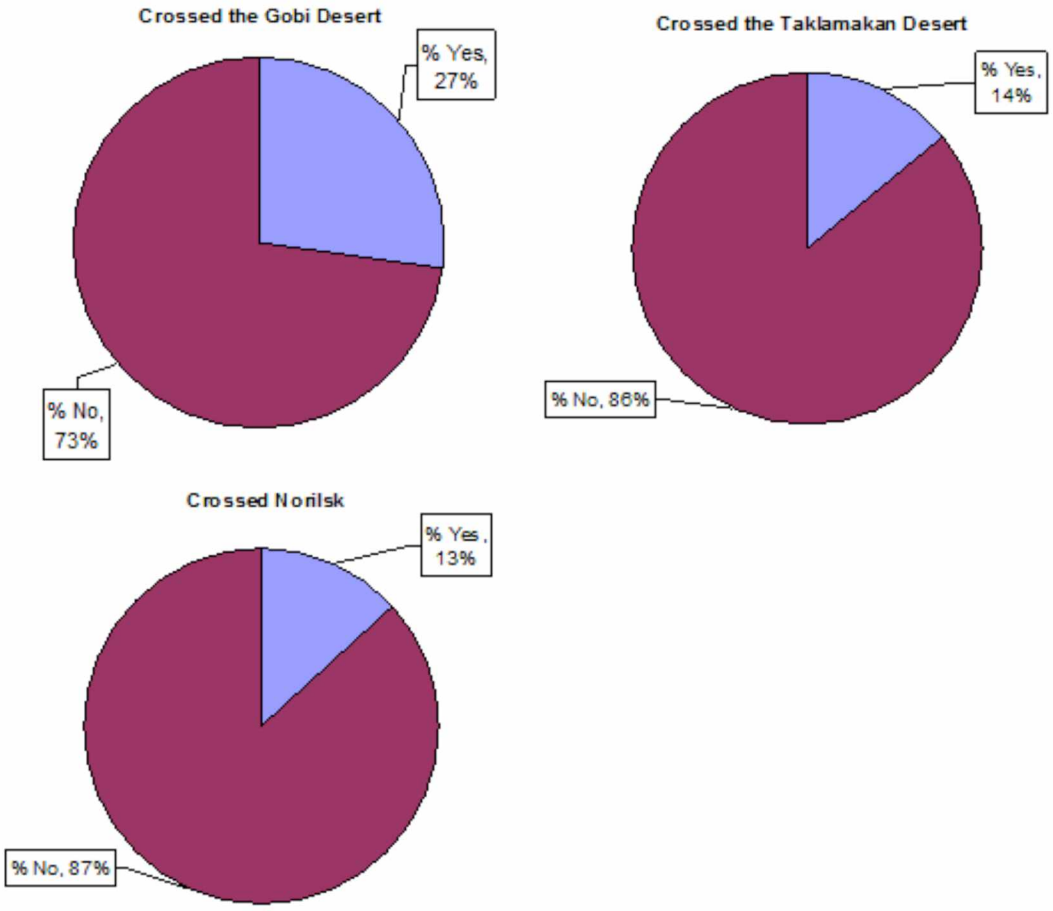

Figure 23. The percentage of time that Trapper Creek trajectories crossed a certain source region during transport.

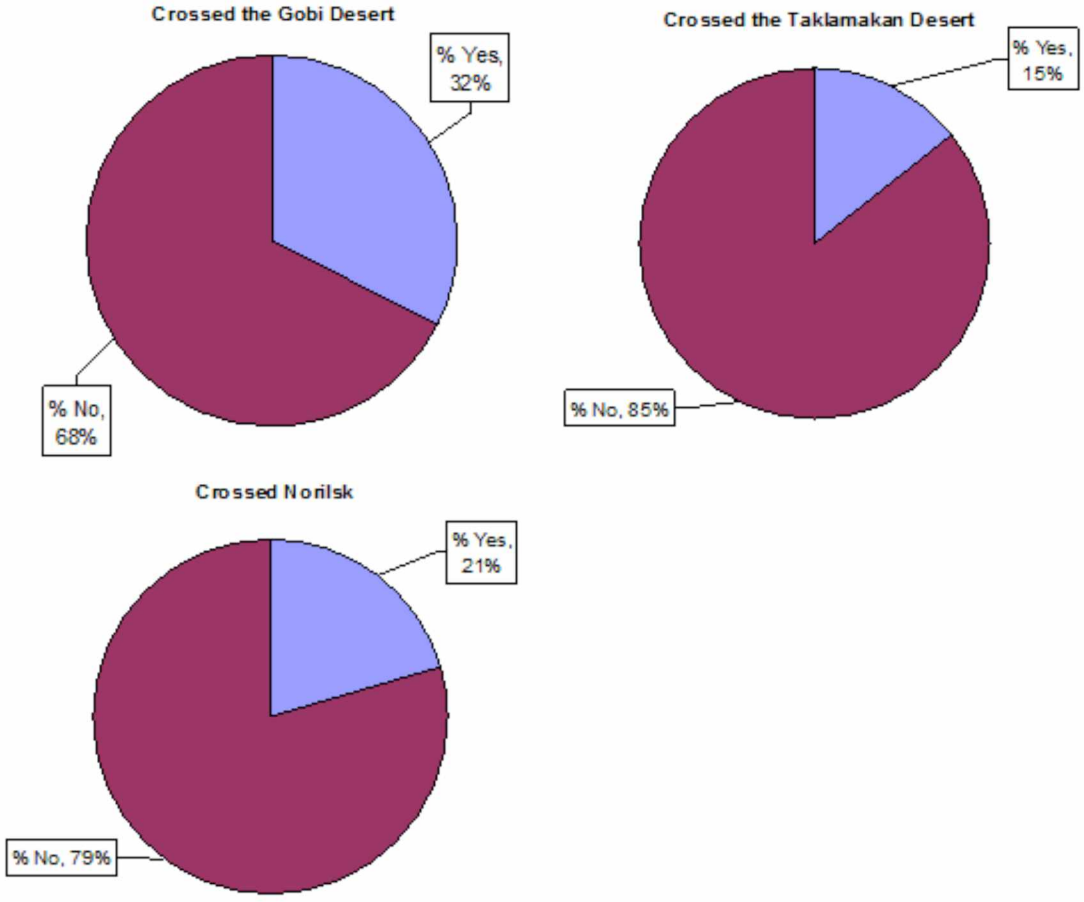

Figure 24. The percentage of time that McGrath trajectories crossed a certain source region during transport.

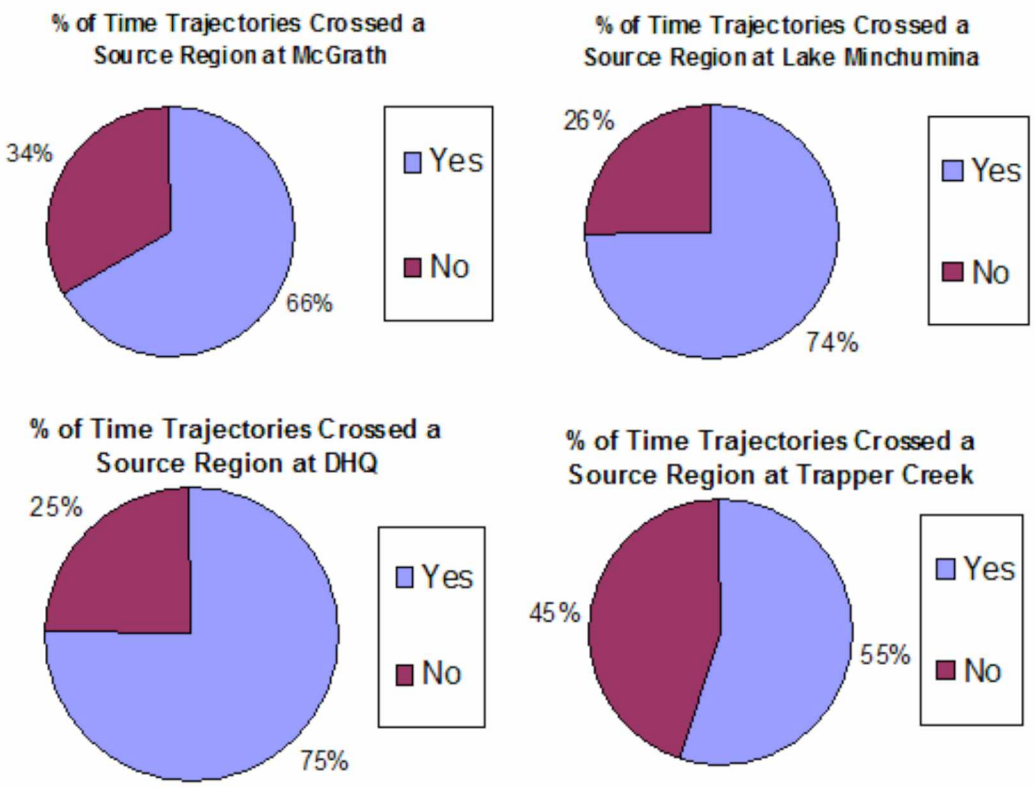

Figure 25. The percentage of time trajectories did not cross a source region versus the percent of time it crossed at least one of the source regions at each site.

3.3 Aerosol Events/HYSPLIT Analysis

To see if there is a comparison between aerosol events (when aerosol concentrations were twice the average for that time frame) and when air parcels pass over possible source regions an analysis that combined the results of the aerosol composition and HYSPIT analyses was done. As described above, HYSPLIT backward trajectories were calculated for each day of the study and used to determine if the air parcel sampled on a given sample day crossed source regions of interest on its way to the site. This data was combined with the aerosol event thresholds to create a table of dates with concentrations above and below the event threshold and whether or not each of these dates had trajectories crossing the source regions of interest. An excerpt of the resulting

data table is shown in table 14. In table 14, any date with a concentration above the event threshold concentration is an event and any date with a concentration below the event threshold is not an event. A '1' in the source region column means that at least one backward trajectory started on that sample date crossed that source region while a '2' means that no backward trajectories started on that sample date crossed that source region.

Table 14. An example of the $PM_{2.5}$ SOIL concentration event chart at DHQ.

Date	Time (HR:MIN AKST)	K Conc. (ng/m^3)	Crossed Gobi	Crossed Taklamakan	Crossed Norilsk
3/14/2009	19:26	242.2	2	2	2
3/7/2009	16:26	242.4	1	2	2
3/14/2009	10:26	245.8	2	2	2
3/3/2009	10:26	251.4	1	1	2
3/13/2009	16:26	253.1	1	2	2
3/7/2009	10:26	253.8	1	2	2
3/1/2009	10:26	257.9	2	2	2
3/8/2009	4:26	263.00	2	2	2
3/6/2009	16:26	268.2	1	2	2
3/5/2009	4:26	269.1	1	1	2
Event Threshold		269.3			
3/7/2009	4:26	270.2	1	2	2
3/1/2009	16:26	271.3	2	2	2
3/9/2009	16:26	273.00	1	2	2
3/2/2009	7:26	273.4	1	1	2
5/12/2009	18:33	273.7	1	2	1
3/8/2009	7:26	274.7	2	2	2
3/7/2009	19:26	277.9	1	2	2
3/9/2009	7:26	288.8	1	2	2
3/2/2009	22:26	291.2	1	1	2
3/3/2009	19:26	291.7	1	1	2

Comparisons between source regions and aerosol events were examined to see if there are similarities on both the events and non-events for each species, for each size, at each location. An example of the statistics is shown in table 15.

Table 15. An example of statistics for SOIL (Size $PM_{2.5}$) in Spring 2009 at DHQ.

Average	134.6			
Event threshold	269.3			
Total # of periods	382			
Event				
	Concentration above event threshold	**Crossed Gobi and above event threshold**	**Crossed Taklamakan and above event threshold**	**Crossed Norilsk and above event threshold**
# of times	29	24	6	1
Percent of total	7.6	6.3	1.6	0.3
Percent of above event threshold	100.0	82.8	20.7	3.4
	Concentration below event threshold	**Crossed Gobi and below event threshold**	**Crossed Taklamakan and below event threshold**	**Crossed Norilsk and below event threshold**
No event				
# of times	353	9	3	0
Percent of total	92.4	2.4	0.8	0
Percent of below event threshold	100	2.5	0.8	0

These comparisons were used to help determine the emission sources impacting DNPP by examining the regions crossed by the air parcels reaching a site and correlating those regions with source emissions characteristics and aerosol composition at a site. Two of the major contributors to RCON, ammonium sulfate and SOIL, were especially useful for identifying aerosols from these source regions. However these are not the only species looked at in this study. Other heavy metals were examined for each of the events. As stated when concentrations of SOIL were at or above event level comparisons

between that and paths of trajectories passing over source regions was looked at. However other elements such as aluminum, iron, silicon, and a few others were also examined for their comparisons with events since they are also soil components elements. When ammonium sulfate concentrations were at or above event levels, comparisons between the elevated levels and the paths of trajectories passing source regions was looked at along with other known industry emitted elements such as sulfur and zinc (figure 26). However since ammonium sulfate and SOIL are the main components of industry and dust respectively they are the ones that will be inspected more thoroughly in the following discussion.

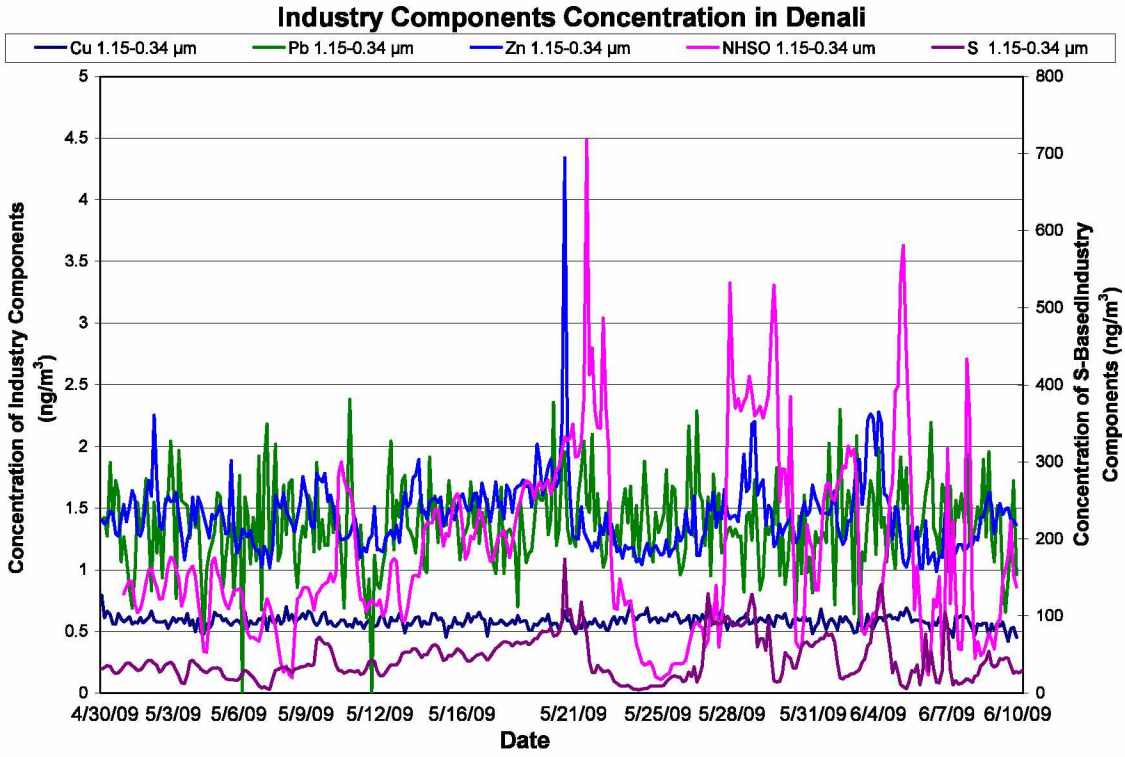

Figure 26. Industrial component concentrations at DNPP.

Ammonium sulfate is a large component of 'industry' pollution due to the combustion of coal and oil and the smelting of metals, both of which emit sulfur dioxide. During transport in the atmosphere the sulfate chemically transforms into ammonium sulfate (Jacob, 1999). Ammonium sulfate is not the only industrial pollution indicator. There are similar peak times in copper, zinc, and lead at the same time as ammonium sulfate which suggests that these parameters are also industrial pollutants. The relationships between ammonium sulfate events and air parcel trajectories crossing the industrial source location of Norilsk, Russia vary with season and site (tables 16-18). During spring 2008, summer 2008 and winter 2008/2009 the percentage of time that a trajectory crosses Norilsk during an event is much higher than during a non-event for all four sites. The high percentage shows that during these seasons the aerosol sources outside of Alaska are more likely to blame for the high aerosol concentrations and associated visibility degradations than local sources. However, in fall 2008, spring 2009, and summer 2009 the percentage of time that a trajectory crosses Norilsk during an event is much higher than during a non-event at DHQ and Lake Minchumina, but not at Trapper Creek and McGrath. Therefore sources outside of Alaska may be to blame for the elevated aerosols at DHQ and Lake Minchumina, but that local aerosol sources may be influencing the aerosol concentrations and visibility at Trapper Creek and McGrath.

However, ammonium sulfate is not only produced by industry. It can be released into the atmosphere directly from volcanic eruptions in the form of SO_2. It can also be produced from marine organisms in the form of dimethyl sulfide. There is also carbonyl sulfide, or OCS, which is emitted from both the oceans, volcanoes, and is produced

anthropogenically (Seinfeld, 2006). Therefore another parameter, zinc, which is known to come from industrial sources, was analyzed to confirm the relationship between high concentrations of ammonium sulfate and air parcels passing over industrial source regions. The zinc concentrations show the same pattern as ammonium sulfate suggesting that the ammonium sulfate is due to industrial emissions.

The other major contributor to RCON was SOIL. SOIL events have different relationships with air parcel trajectories that cross the Gobi and Taklamakan Deserts depending on the season and the site. During fall 2008 and Winter 2008/2009 the percentage of time that a trajectory crosses one of the deserts during an event is much higher than during a non-event for all four sites. The higher percentages shows that during Fall 2008 and Winter 2008/2009 sources outside of Alaska are more likely to blame for the high aerosol concentration and the associated decrease in visibility than local sources during a period of elevated SOIL which makes sense because Alaska is snow covered during these times so local dust emissions should be low. During Spring 2008, Summer 2008, and Summer 2009 the percentage of time that a trajectory crosses one of the deserts during a SOIL event is about the same as during a non-event, with a few exceptions which shows that both sources outside of Alaska and local sources are to blame for visibility degradation during the high SOIL events seen during these periods. In Spring 2009, the measurements at DHQ showed a percentage of time that a trajectory crosses one of the deserts during an event that was much higher than during a non-event, implying a SOIL source outside of Alaska. However, the measurements at Lake Minchumina showed the opposite situation, implying that its local sources are more at

fault for the high concentrations of SOIL than outside sources. The other two sites had too little data during this period to do any comparisons and determine the regional/local nature of the effects seen at Lake Minchumina.

Table 16. Percentage of time when HYSPLIT trajectories crossed Norilsk, Russia and reached a sampling site during an elemental peak in ammonium sulfate. Data in italics indicates that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Norilsk Industry (S) Event						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*0*	14	17	*50*	*0*	N/D
Large (1.15-2.5 µm)	*0*	17	4	*4*	*0*	N/D
Medium (0.34-1.15 µm)	*33*	15	25	*50*	*0*	N/D
Small (0.1-0.34 µm)	*0*	12	22	*38*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*0*	2	31	20	*0*	N/D
Large (1.15-2.5 µm)	*0*	0	18	24	*0*	N/D
Medium (0.34-1.15 µm)	*0*	6	36	19	*0*	N/D
Small (0.1-0.34 µm)	*0*	0	28	23	*0*	N/D
Denali						
PM 2.5	4	52	38	29	7	*37*
Large (1.15-2.5 µm)	1	59	23	24	7	*31*
Medium (0.34-1.15 µm)	4	41	38	27	16	*34*
Small (0.1-0.34 µm)	4	44	37	29	0	*32*
Trapper Creek						
$PM_{2.5}$	N/D	*0*	3	N/D	*0*	*15*
Large (1.15-2.5 µm)	N/D	*0*	3	N/D		*0*
Medium (0.34-1.15 µm)	N/D	*0*	8	N/D	*0*	*16*
Small (0.1-0.34 µm)	N/D	*0*	0	N/D	*0*	*11*

Table 17. Percentage of time when HYSPLIT trajectories did not cross Norilsk, Russia and reached a sampling site during an elemental peak in ammonium sulfate. Data in italics indicates that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Norilsk Industry (S) Non-event statistics						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*0*	2	36	*0*	*0*	N/D
Large (1.15-2.5 µm)	*0*	3	36	*0*	*0*	N/D
Medium (0.34-1.15 µm)	*0*	2	35	*0*	*0*	N/D
Small (0.1-0.34 µm)	*0*	2	36	*0*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*0*	0	3	26	*0*	N/D
Large (1.15-2.5 µm)	*0*	2	16	19	*0*	N/D
Medium (0.34-1.15 µm)	*0*	0	3	17	*0*	N/D
Small (0.1-0.34 µm)	*0*	1	22	39	*0*	N/D
Denali						
PM 2.5	7	0	22	0	13	*0*
Large (1.15-2.5 µm)	17	0	29	0	14	*0*
Medium (0.34-1.15 µm)	8	0	12	0	14	*0*
Small (0.1-0.34 µm)	3	0	31	0	13	*3*
Trapper Creek						
$PM_{2.5}$	N/D	*0*	29	N/D	*14*	*15*
Large (1.15-2.5 µm)	N/D	*0*	52	N/D	*0*	*14*
Medium (0.34-1.15 µm)	N/D	*0*	31	N/D	*5*	*11*
Small (0.1-0.34 µm)	N/D	*0*	42	N/D	*0*	*26*

Table 18. Percentage of time when HYSPLIT trajectories crossed Norilsk, Russia and reached a sampling site during an elemental peak in zinc. Data in italics indicate that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Norilsk Industry (Zn) Event statistics						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*0*	4	12	*23*	*0*	N/D
Large (1.15-2.5 µm)	*0*	100	3	*19*	*0*	N/D
Medium (0.34-1.15 µm)	*80*	0	25	*8*	*0*	N/D
Small (0.1-0.34 µm)	*100*	4	11	*10*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*0*	18	13	14	*0*	N/D
Large (1.15-2.5 µm)	*0*	21	7	19	*100*	N/D
Medium (0.34-1.15 µm)	*0*	15	6	13	*11*	N/D
Small (0.1-0.34 µm)	*0*	0	20	22	*0*	N/D
Denali						
$PM_{2.5}$	8	31	27	32	0	*47*
Large (1.15-2.5 µm)	14	25	25	22	0	*38*
Medium (0.34-1.15 µm)	6	10	39	28	24	*36*
Small (0.1-0.34 µm)	10	57	0	14	0	*35*
Trapper Creek						
$PM_{2.5}$	N/D	*0*	14	N/D	*0*	*9*
Large (1.15-2.5 µm)	N/D	*23*	18	N/D	*0*	*0*
Medium (0.34-1.15 µm)	N/D	*0*	17	N/D	*0*	*9*
Small (0.1-0.34 µm)	N/D	*0*	14	N/D	*0*	*6*

Table 19. Percentage of time when HYSPLIT trajectories did not cross Norilsk, Russia and reached a sampling site during an elemental peak in zinc. Data in italics indicate that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Norilsk Industry (Zn) Non-event statistics						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*0*	10	33	*0*	*0*	N/D
Large (1.15-2.5 µm)	*0*	0	41	*0*	*0*	N/D
Medium (0.34-1.15 µm)	*0*	29	27	*0*	*0*	N/D
Small (0.1-0.34 µm)	*0*	17	42	*0*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*0*	21	9	11	*50*	N/D
Large (1.15-2.5 µm)	*0*	13	40	3	*0*	N/D
Medium (0.34-1.15 µm)	*0*	11	17	18	*22*	N/D
Small (0.1-0.34 µm)	*0*	25	9	41	*67*	N/D
Denali						
$PM_{2.5}$	15	2	13	0	0	*0*
Large (1.15-2.5 µm)	21	14	0	0	0	*0*
Medium (0.34-1.15 µm)	5	0	12	2	0	*0*
Small (0.1-0.34 µm)	9	0	9	5	0	*15*
Trapper Creek						
$PM_{2.5}$	N/D	*0*	11	N/D	*14*	*9*
Large (1.15-2.5 µm)	N/D	*0*	21	N/D	*10*	*5*
Medium (0.34-1.15 µm)	N/D	*0*	21	N/D	*11*	*5*
Small (0.1-0.34 µm)	N/D	*25*	24	N/D	*0*	*18*

Table 20. Percentage of time when HYSPLIT trajectories crossed the Gobi desert and reached a sampling site during an elemental peak in 'SOIL'. Data in italics indicate that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Gobi Desert (SOIL) Event Statistics						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*50*	11	15	*67*	*0*	N/D
Large (1.15-2.5 µm)	*50*	14	21	*70*	*0*	N/D
Medium (0.34-1.15 µm)	*50*	12	31	*33*	*0*	N/D
Small (0.1-0.34 µm)	*50*	5	10	*27*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*0*	54	55	93	*0*	N/D
Large (1.15-2.5 µm)	*0*	54	28	87	*0*	N/D
Medium (0.34-1.15 µm)	*20*	25	54	77	*100*	N/D
Small (0.1-0.34 µm)	*83*	45	70	92	*0*	N/D
Denali						
$PM_{2.5}$	40	9	37	98	83	*18*
Large (1.15-2.5 µm)	45	8	38	95	83	*18*
Medium (0.34-1.15 µm)	25	6	45	84	53	*12*
Small (0.1-0.34 µm)	42	22	20	90	71	*16*
Trapper Creek						
$PM_{2.5}$	N/D	*35*	58	N/D	*11*	*20*
Large (1.15-2.5 µm)	N/D	*25*	51	N/D	*17*	*16*
Medium (0.34-1.15 µm)	N/D	*25*	39	N/D	*23*	*44*
Small (0.1-0.34 µm)	N/D	*25*	55	N/D	*6*	*43*

Table 21. Percentage of time when HYSPLIT trajectories did not cross the Gobi desert and reached a sampling site during an elemental peak in 'SOIL'. Data in italics indicate that the season had less than a month's worth of data and that the percentage may have been skewed as a result. N/D indicates no data for that time period/site.

Gobi Desert (SOIL) Non-event Statistics						
Size/ Season	Spring 2008	Summer 2008	Fall 2008	Winter 2008/2009	Spring 2009	Summer 2009
McGrath						
$PM_{2.5}$	*0*	12	28	*0*	*0*	N/D
Large (1.15-2.5 µm)	*0*	13	33	*30*	*0*	N/D
Medium (0.34-1.15 µm)	*50*	16	27	*0*	*0*	N/D
Small (0.1-0.34 µm)	*100*	27	33	*0*	*0*	N/D
Lake Minchumina						
$PM_{2.5}$	*50*	6	32	69	*0*	N/D
Large (1.15-2.5 µm)	*20*	4	21	32	*0*	N/D
Medium (0.34-1.15 µm)	*50*	4	38	81	*100*	N/D
Small (0.1-0.34 µm)	*0*	5	17	48	*0*	N/D
Denali						
$PM_{2.5}$	40	39	21	57	31	*30*
Large (1.15-2.5 µm)	48	30	24	63	33	*25*
Medium (0.34-1.15 µm)	44	18	22	63	29	*17*
Small (0.1-0.34 µm)	63	56	7	52	44	*16*
Trapper Creek						
$PM_{2.5}$	N/D	*24*	22	N/D	*58*	*20*
Large (1.15-2.5 µm)	N/D	*25*	40	N/D	*56*	*16*
Medium (0.34-1.15 µm)	N/D	*17*	13	N/D	*54*	*11*
Small (0.1-0.34 µm)	N/D	*13*	17	N/D	*33*	*7*

The above analysis suggests that during a majority of the year outside sources had a significant impact on aerosol concentrations and visibility in DNPP. The next question is what are the specific source types that produce the observed aerosols and to address this question, a CMB analysis was performed on the aerosol concentrations.

3.4 CMB Analysis Results

The CMB model program was run for days identified in the aerosol concentrations as having the highest ten or lowest ten concentrations for the soil (SOIL) and industry-related species (ammonium sulfate). The results of the model showed a combination of potential emission sources that could be responsible for the observed aerosol composition. How many times these sources appeared during the highest and lowest concentration days per season and site are shown in figures 27 - 50 for industry and 51 - 74 for SOIL. An event occurs when a parameter's concentration is twice the average for the parameter during the specified time frame, in this case the season. Therefore, non-event days are when a parameter's concentration is below twice the average for the parameter during the specified time frame, in this case, the season. If there is an N/A it means that there was no data for that season available.

During ammonium sulfate/zinc (industry) events, the CMB results showed that the sources were dominated by secondary ammonium sulfate (not specific to a given aerosol emission source profile and usually due to sulfur dioxide gas conversion into ammonium sulfate), industrial sources (factories, coal-fire power plants) and oil combustion (figures 27-50). During ammonium sulfate non-event days, the CMB results showed that sources were mainly vehicle exhaust, marine components such as sea salt

and oil combustion (figures 27-50). Overall this data suggests that different sources are producing the ammonium sulfate observed during an ammonium sulfate peak than during an ammonium sulfate low. Industry and power generation appear to be the major contributors during a peak in ammonium sulfate concentration and vehicles, oil combustion and sea spray are the major RCON contributors during period of low ammonium sulfate concentrations. For peaks in the industrial species the ammonium sulfate was responsible for 59% to 78% of RCON on any given day in Denali, 54% to 79% of RCON on any given day in Lake Minchumina, 60% to 79% of RCON on any given day in Trapper Creek, 38% to 73% of RCON on any given day in McGrath. As one can see the four sites are fairly similar with the CMB results no matter the amount of data available and between seasons.

As stated before During spring 2008, summer 2008 and winter 2008/2009 the percentage of time that a trajectory crosses Norilsk during an event is much higher than during a non-event for all four sites. With the percentage of time that a trajectory crosses Norilsk during an event being much higher than during a non-event for all four sites shows that during these seasons the aerosol sources outside of Alaska are more likely to blame for the high aerosol concentrations than local sources. However, in fall 2008, spring 2009, and summer 2009 the percentage of time that a trajectory crosses Norilsk during an event is much higher than during a non-event at DHQ and Lake Minchumina, but not at Trapper Creek and McGrath. The higher percentages at these sites show that sources outside of Alaska may be to blame for the elevated aerosols at DHQ and Lake Minchumina, but that local aerosol sources may be influencing the aerosol concentrations

at Trapper Creek and McGrath. The CMB results during spring 2008, summer 2008 and winter 2008/2009 show that ammonium sulfate is one of, if not, the top source during event times. In fall 2008, spring 2009, and summer 2009, when the trajectory statistics is not as high as other times of the year, the CMB results still show that ammonium sulfate is one of, if not, the top source during event times. Besides one season, the CMB results show that the main source is ammonium sulfate, with the percentage of time source appears in CMB results always above 71%. On the other end, during a non-event ammonium sulfate is not a main source according to CMB with the highest percentage of time source appears in CMB results being 51%, most percentages being in the 20% area which matches data of non-events and trajectories crossing Norilsk.

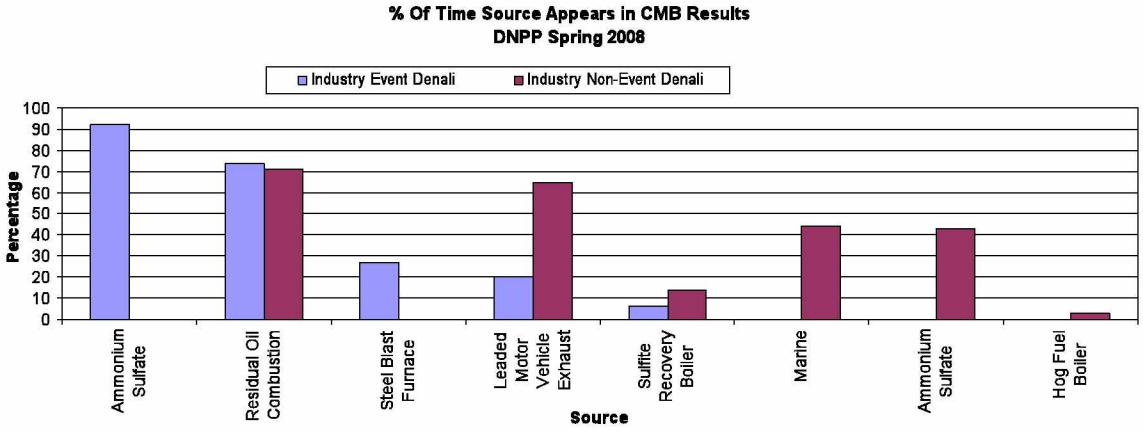

Figure 27. CMB results for DNPP during 'industry' events and non-events, spring 2008.

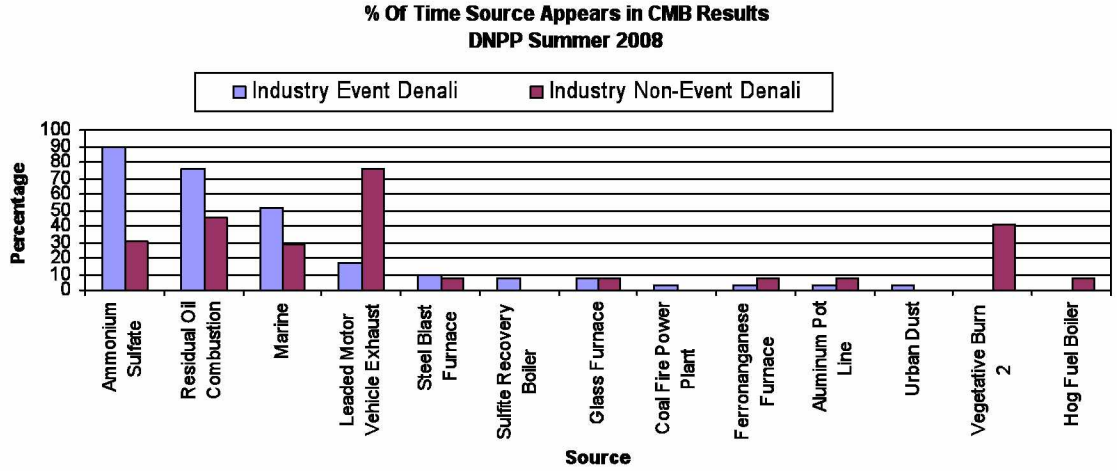

Figure 28. CMB results for DNPP during 'industry' events and non-events, summer 2008.

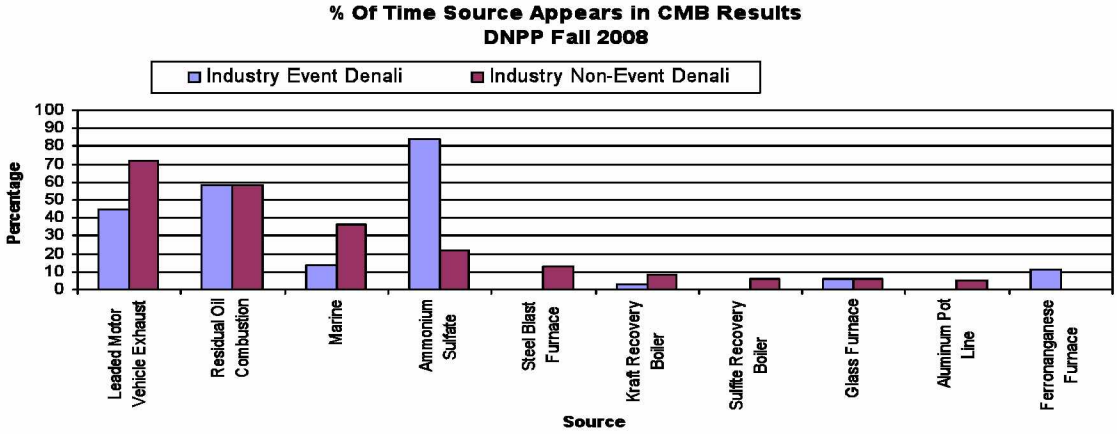

Figure 29. CMB results for DNPP during 'industry' events and non-events, fall 2008.

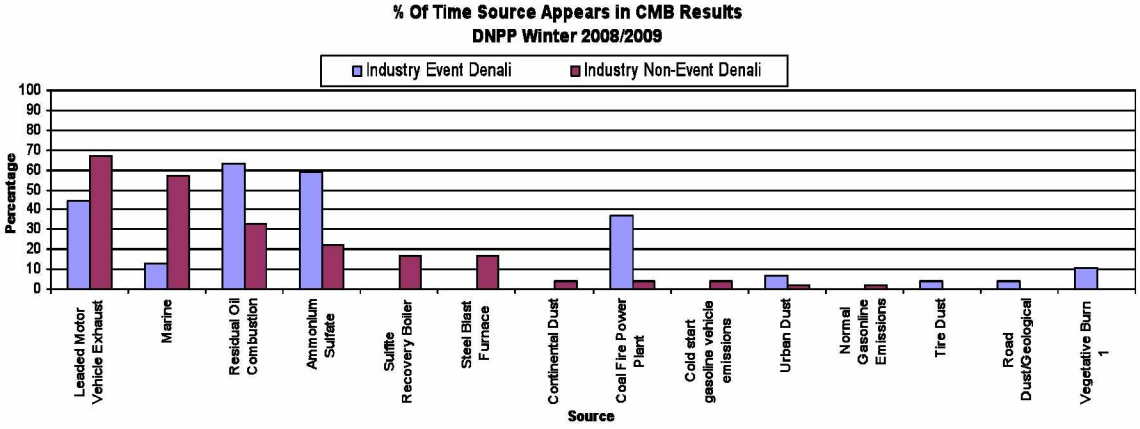

Figure 30. CMB results for DNPP during 'industry' events and non-events, winter 2008/2009.

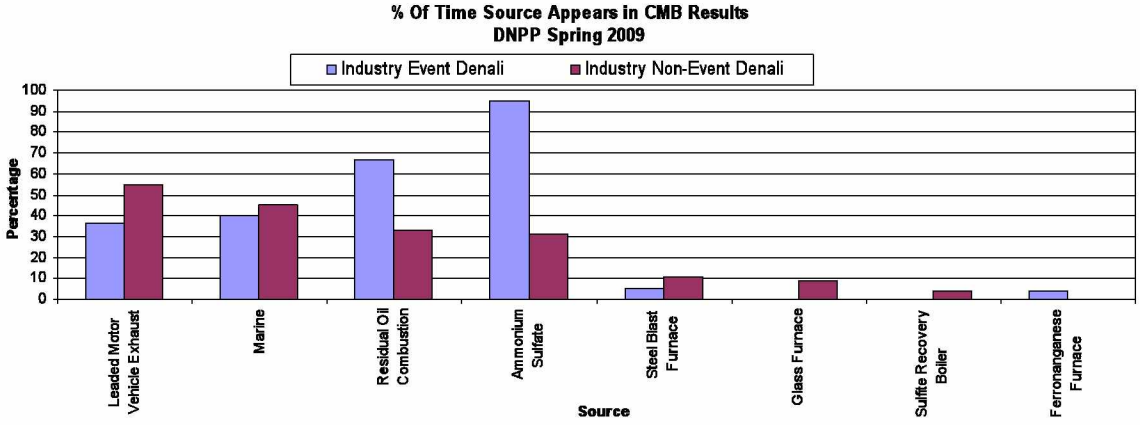

Figure 31. CMB results for DNPP during 'industry' events and non-events, spring 2009.

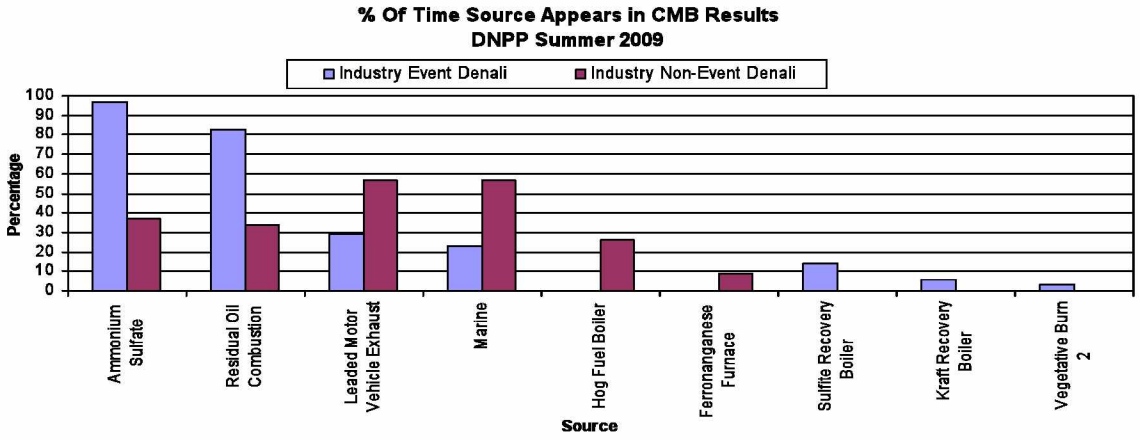

Figure 32. CMB results for DNPP during 'industry' events and non-events, summer 2009.

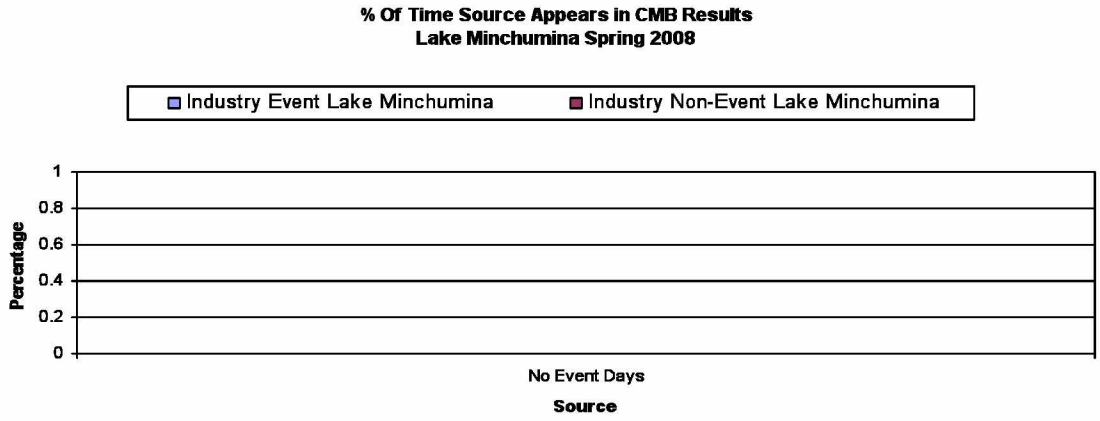

Figure 33. CMB results for Lake Minchumina during 'industry' events and non-events, spring 2008.

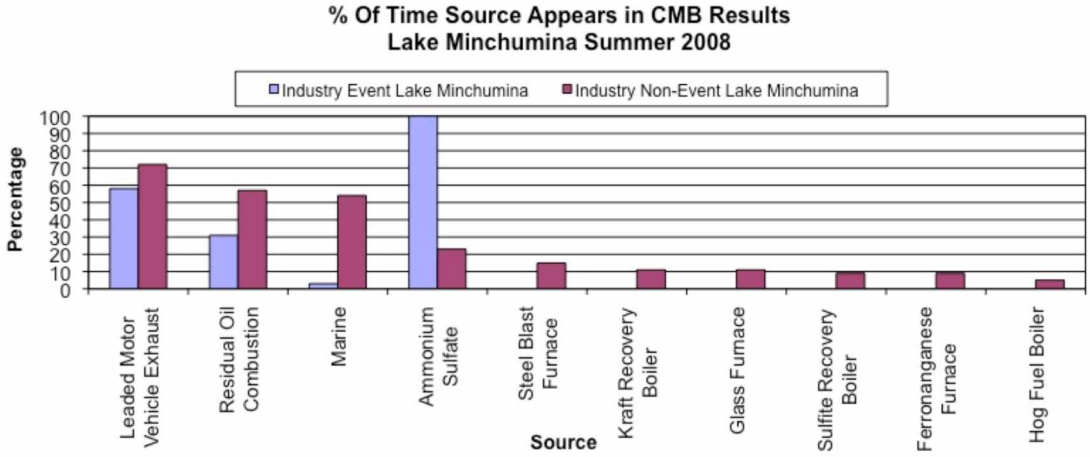

Figure 34. CMB results for Lake Minchumina during 'industry' events and non-events, summer 2008.

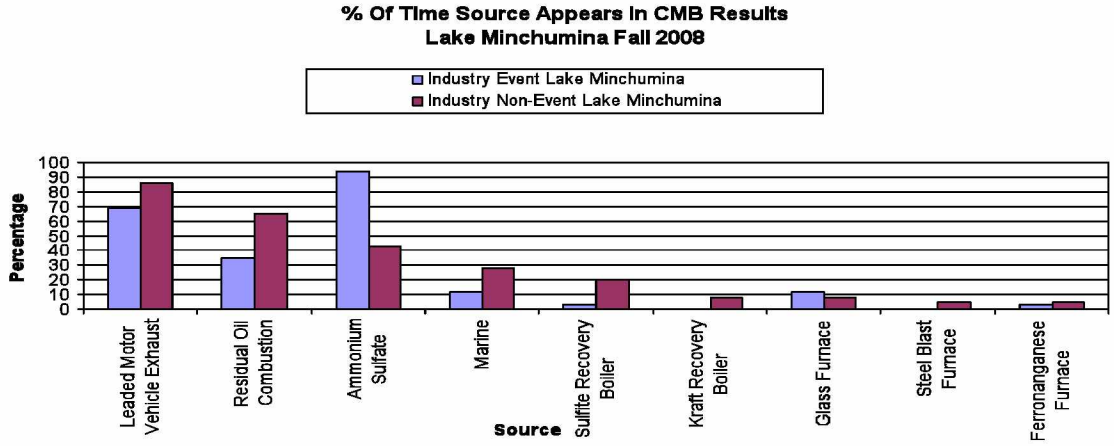

Figure 35. CMB results for Lake Minchumina during 'industry' events and non-events, fall 2008.

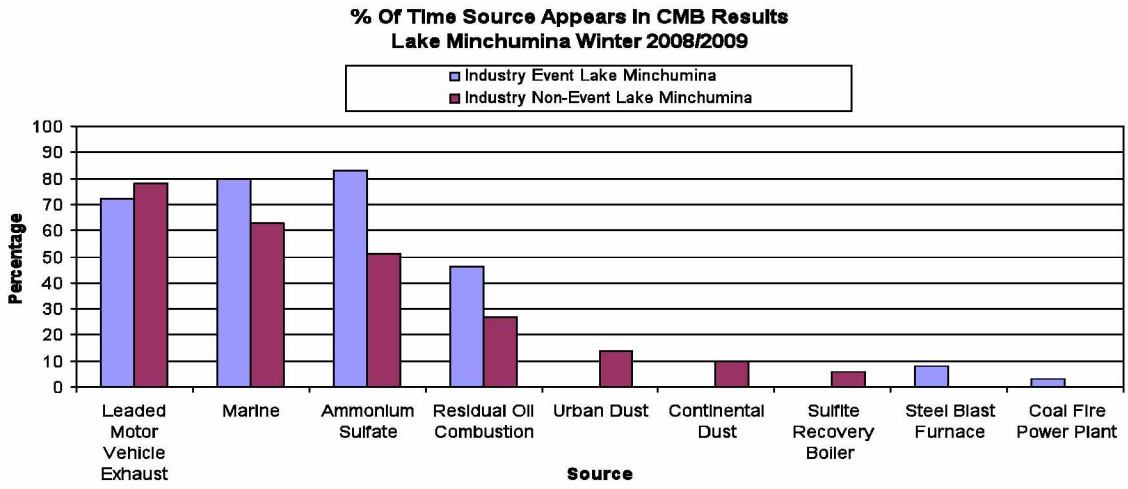

Figure 36. CMB results for Lake Minchumina during 'industry' events and non-events, winter 2008/2009.

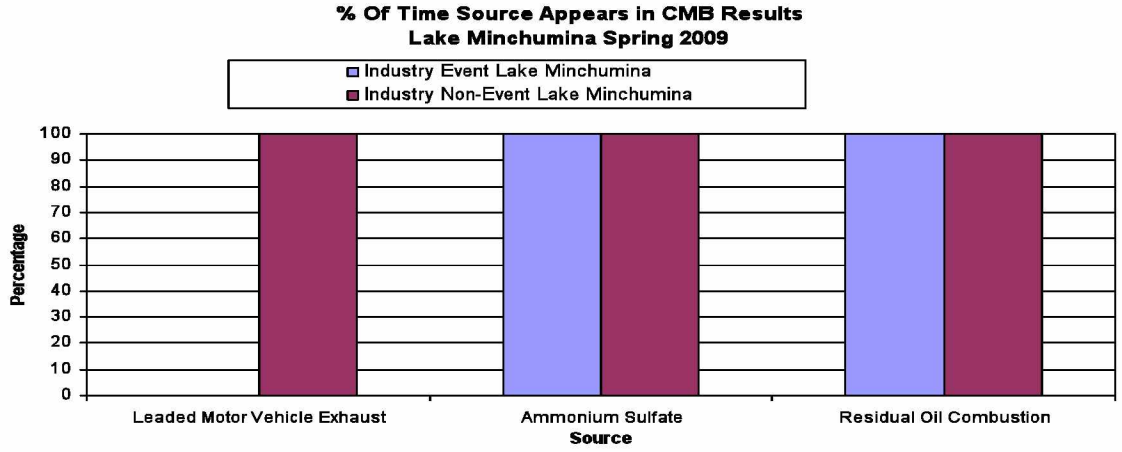

Figure 37. CMB results for Lake Minchumina during 'industry' events and non-events, spring 2009.

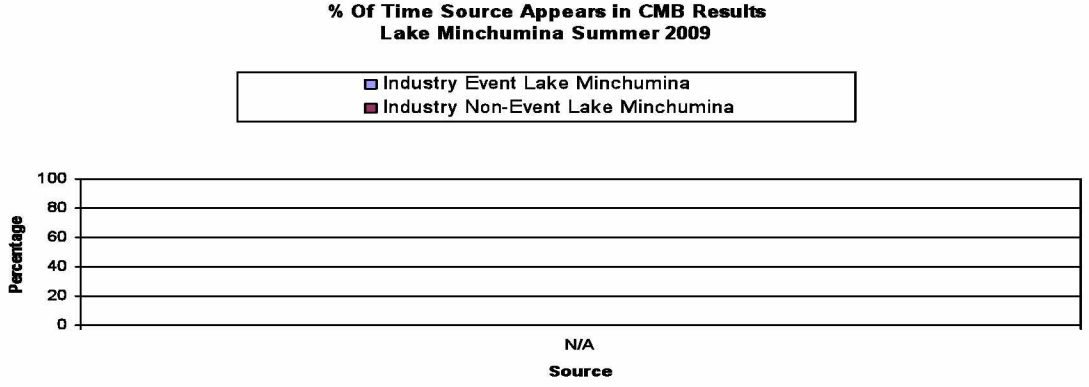

Figure 38. CMB results for Lake Minchumina during 'industry' events and non-events, summer 2009.

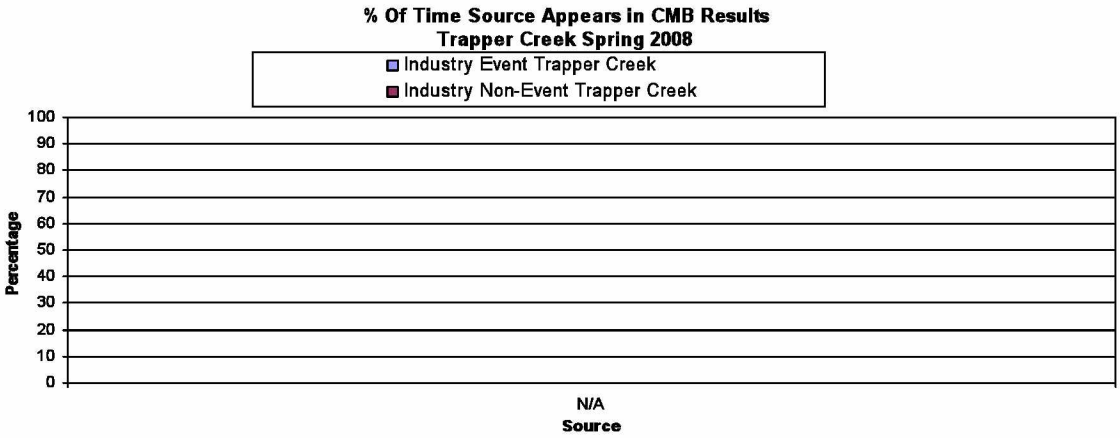

Figure 39. CMB results for Trapper Creek during 'industry' events and non-events, spring 2008.

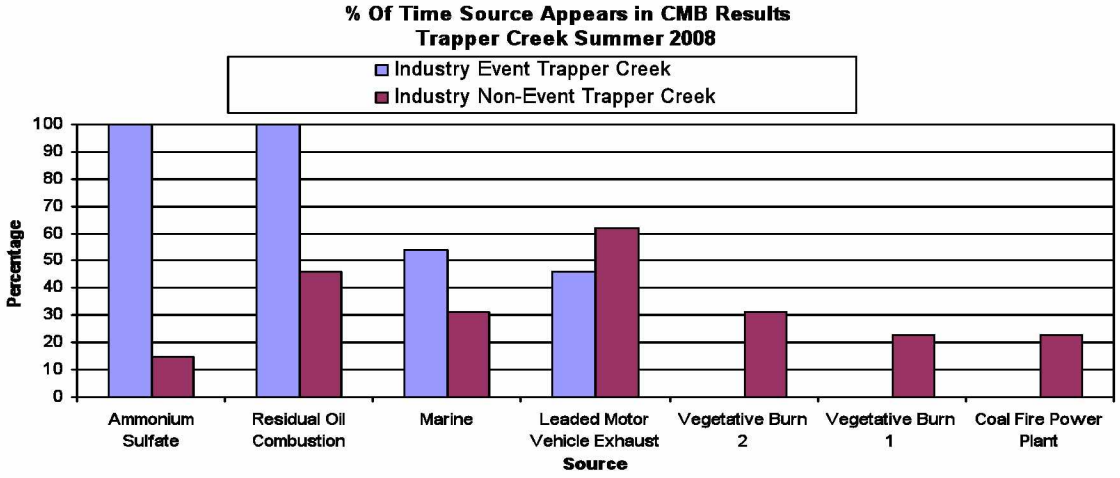

Figure 40. CMB results for Trapper Creek during 'industry' events and non-events, summer 2008.

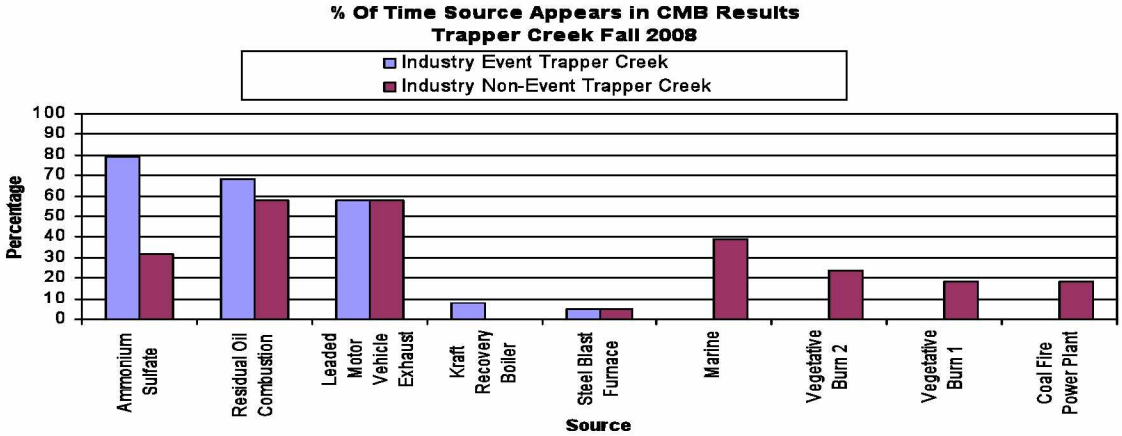

Figure 41. CMB results for Trapper Creek during 'industry' events and non-events, fall 2008.

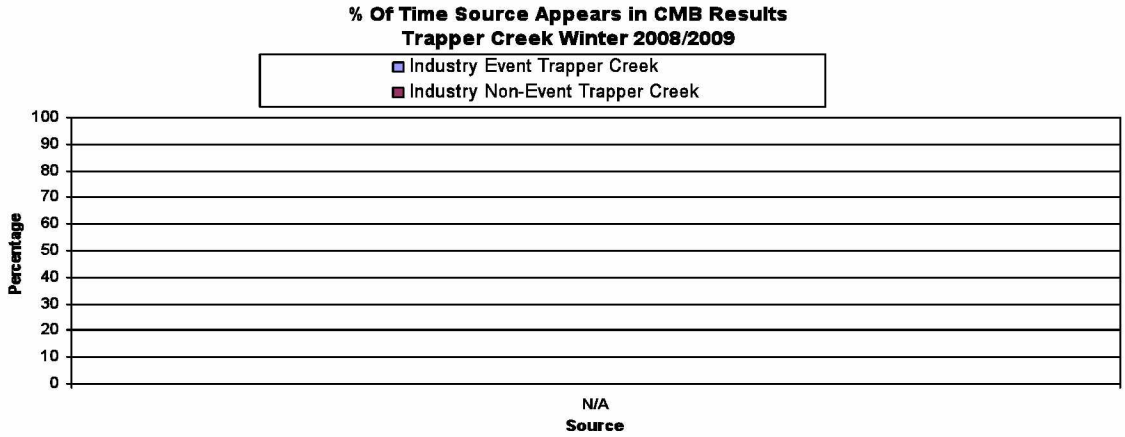

Figure 42. CMB results for Trapper Creek during 'industry' events and non-events, winter 2008/2009.

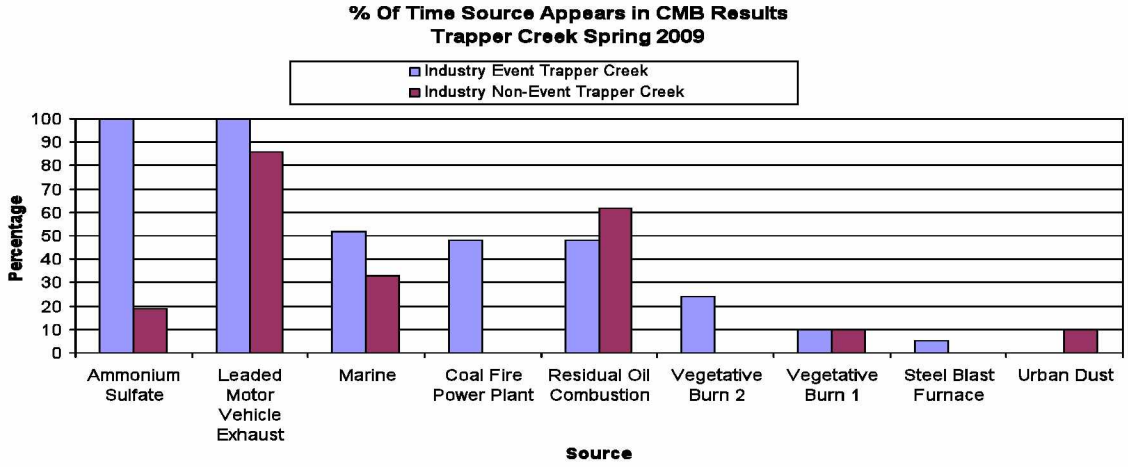

Figure 43. CMB results for Trapper Creek during 'industry' events and non-events, spring 2009.

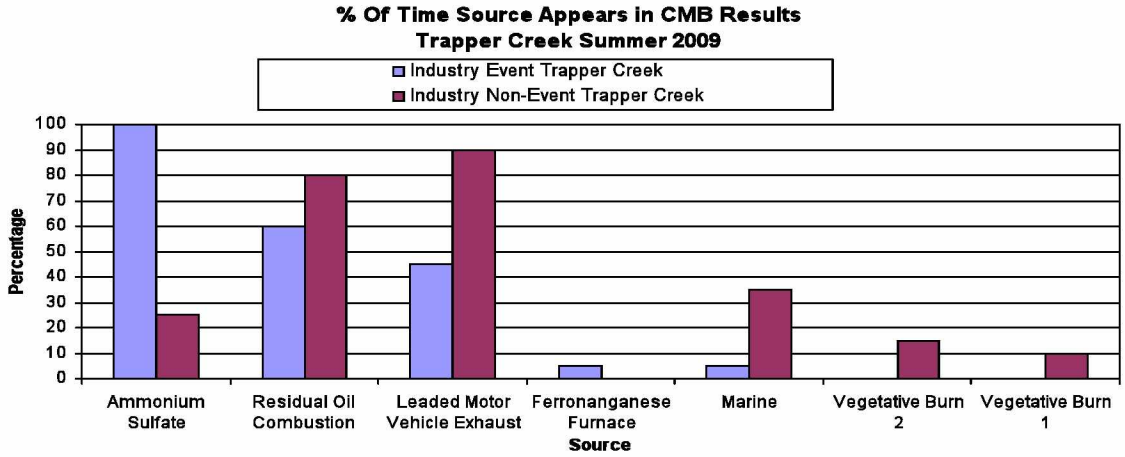

Figure 44. CMB results for Trapper Creek during 'industry' events and non-events, summer 2009.

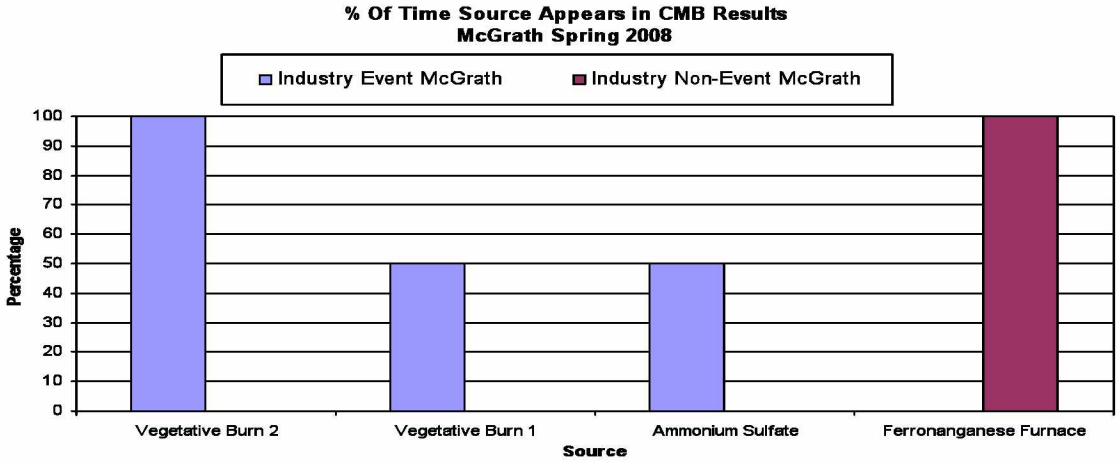

Figure 45. CMB results for McGrath during 'industry' events and non-events, spring 2008.

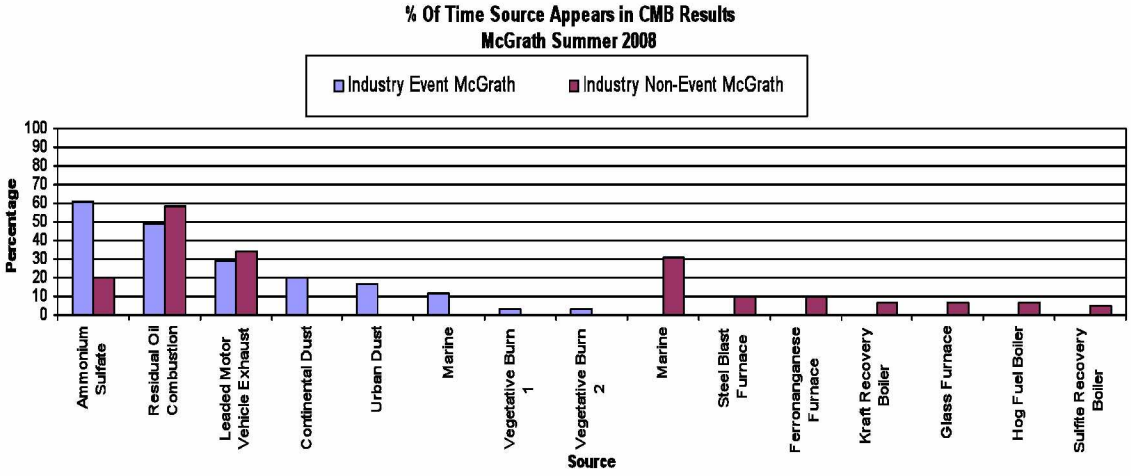

Figure 46. CMB results for McGrath during 'industry' events and non-events, summer 2008.

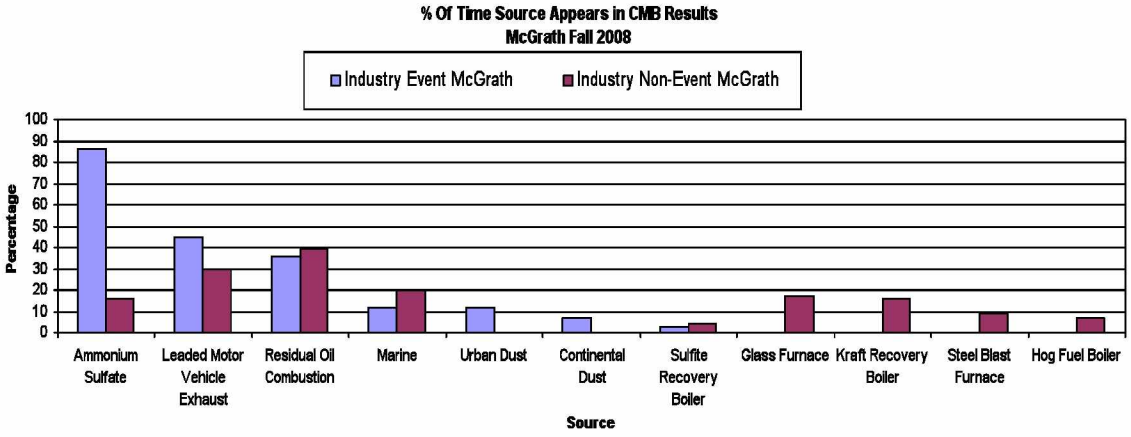

Figure 47. CMB results for McGrath during 'industry' events and non-events, fall 2008.

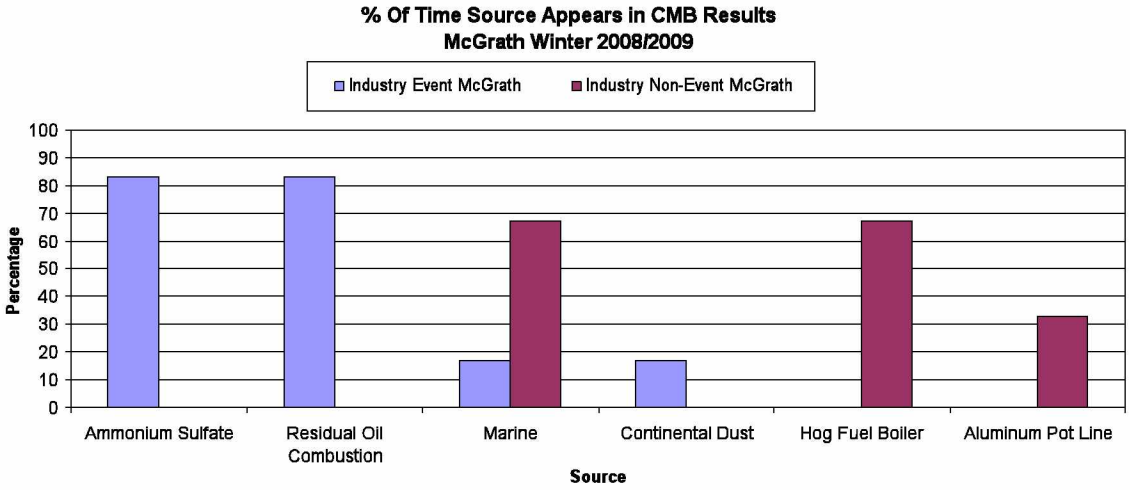

Figure 48. CMB results for McGrath during 'industry' events and non-events, winter 2008/2009.

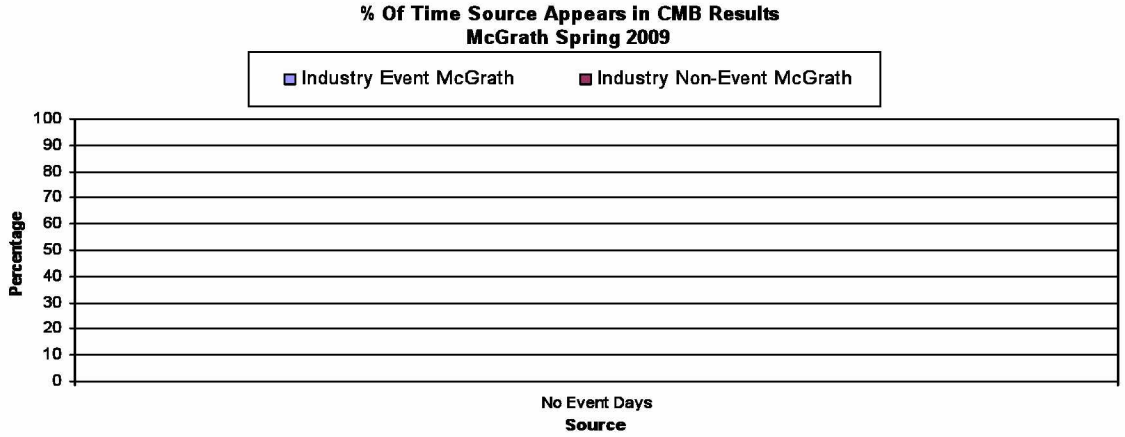

Figure 49. CMB results for McGrath during 'industry' events and non-events, spring 2009.

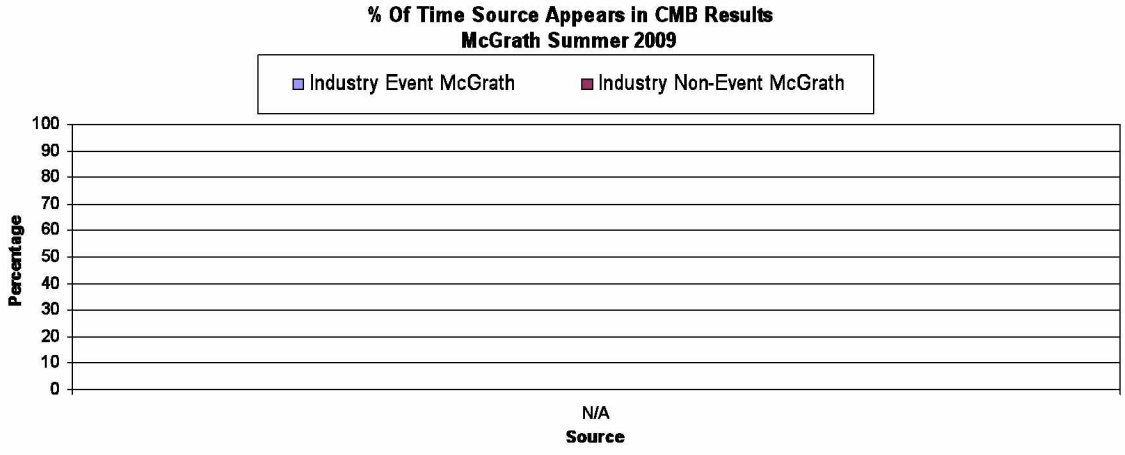

Figure 50. CMB results for McGrath during 'industry' events and non-events, summer 2009.

Below are charts that show the CMB comparison results between SOIL concentrations and soil source profiles. Again an event occurs when a parameter's concentration is twice the average for the parameter during the specified time frame, in this case the season, a non-event days are when a parameter's concentration is below twice the average for the parameter during the specified time frame, and if there is an N/A it means that there was no data for that season available.

Unlike the industry results, the CMB results showed that the sources contributing to SOIL peaks were mainly soil, 'dust' (figures 51 - 74). However, many source profiles have a large soil component with only a few trace species specific to the location where the dust profile was collected separating them. Therefore, the presence of soil in the sample shows up in several different source categories: Road Dust/Geological Dust, Urban Dust, Continental Dust, and Brake Dust. When the SOIL concentration was low, the CMB results showed that the main sources contributing to RCON were mainly coal-fired power plants, motor vehicle exhaust, sea salt, and oil combustion (figures 51 - 74). So, during a SOIL event dust, such as from a desert, is the main contributor to RCON and during a SOIL non-event it is industry and sea-spray. For peaks in the SOIL species the ammonium sulfate was responsible for 20% to 34% of RCON on any given day in Denali, 11% to 45% of RCON on any given day in Lake Minchumina, 21% to 38% of RCON on any given day in Trapper Creek, 19% to 63% of RCON on any given day in McGrath.

As stated before during fall 2008 and Winter 2008/2009 the percentage of time that a trajectory crosses one of the deserts during an event is much higher than during a

non-event for all four sites and during spring 2008, summer 2008, and summer 2009 the percentage of time that a trajectory crosses one of the deserts during a SOIL event is about the same as during a non-event, with a few exceptions. Again high percentages of crossing a source during an event ties in well with the CMB results. During fall 2008 and winter 2008/2009 road/geological dust is the top source for $PM_{2.5}$ followed closely by other dust sources such as urban and continental dust. During spring 2008, summer 2008, and summer 2009 dust sources are in the top sources but at a lower percentage of time source appears in CMB results than in the fall 2008 and winter 2008/2009 seasons. These higher percentages during an event correlates well with the facts - when there is an event, the percentage of time trajectories cross deserts specifically the Gobi and the Taklamakan, is high, and the CMB states the sources are geological dust. When there is not an event, the percentage of time trajectories cross deserts specifically the Gobi and the Taklamakan, is lower, and the CMB states the sources are not dust sources, such as vegetative burn and oil combustion.

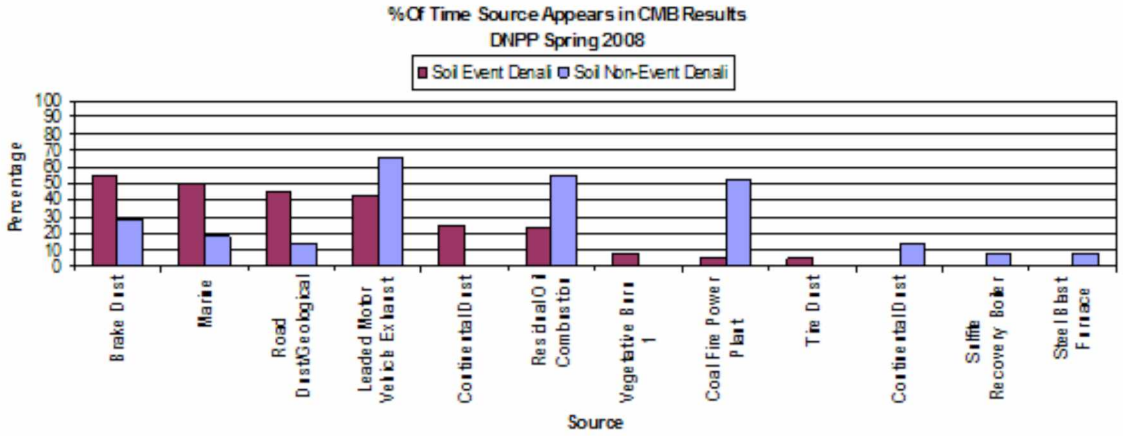

Figure 51. CMB results for DNPP during SOIL events and non-events, spring 2008.

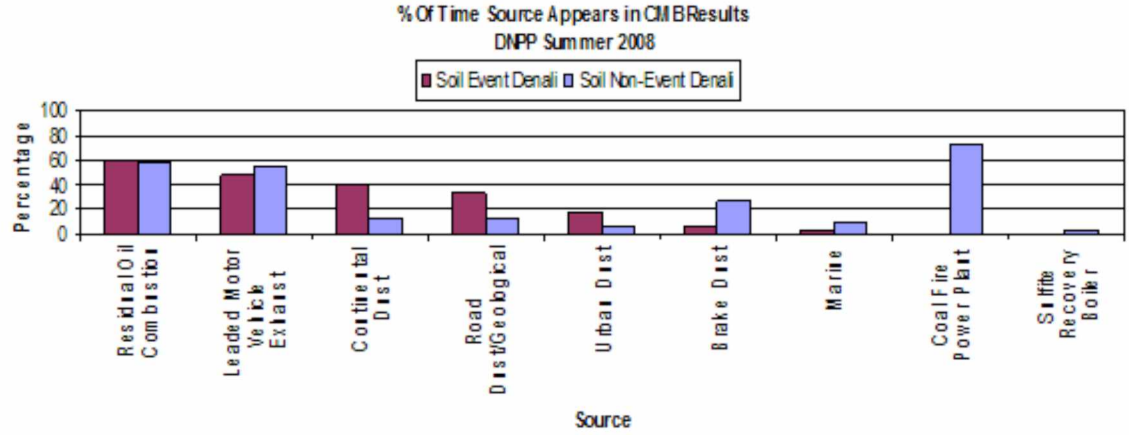

Figure 52. CMB results for DNPP during SOIL events and non-events, summer 2008.

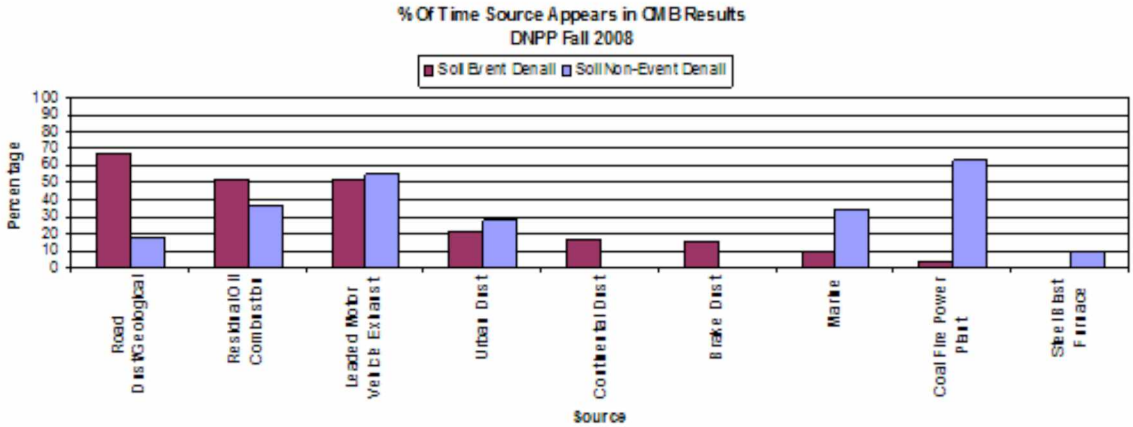

Figure 53. CMB results for DNPP during SOIL events and non-events, fall 2008.

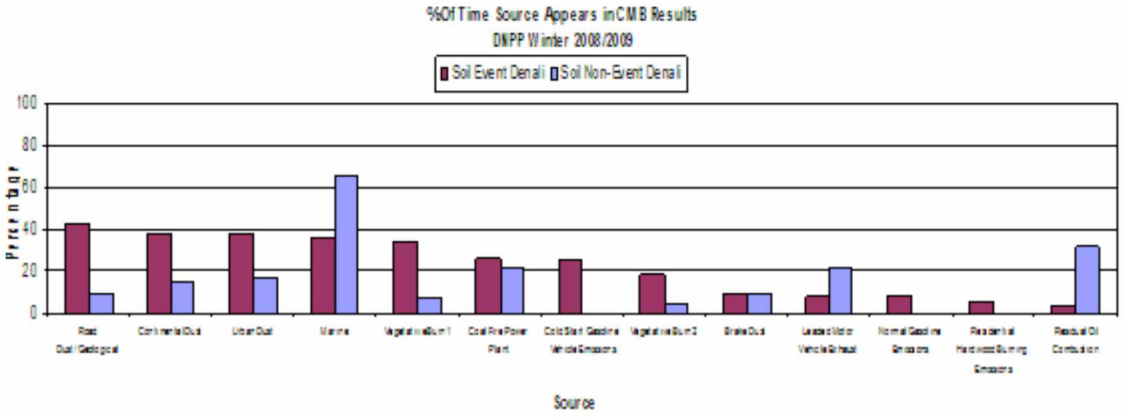

Figure 54. CMB results for DNPP during SOIL events and non-events, winter 2008/2009.

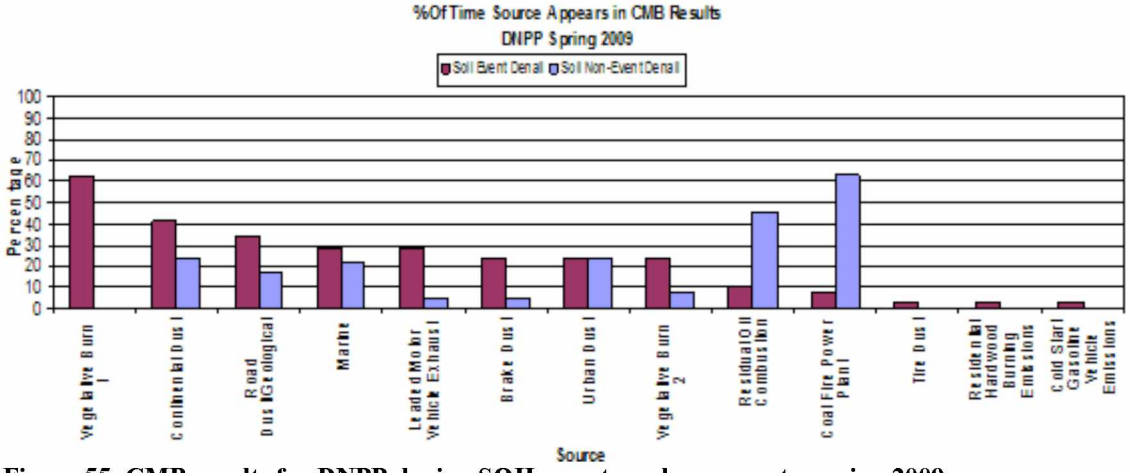

Figure 55. CMB results for DNPP during SOIL events and non-events, spring 2009.

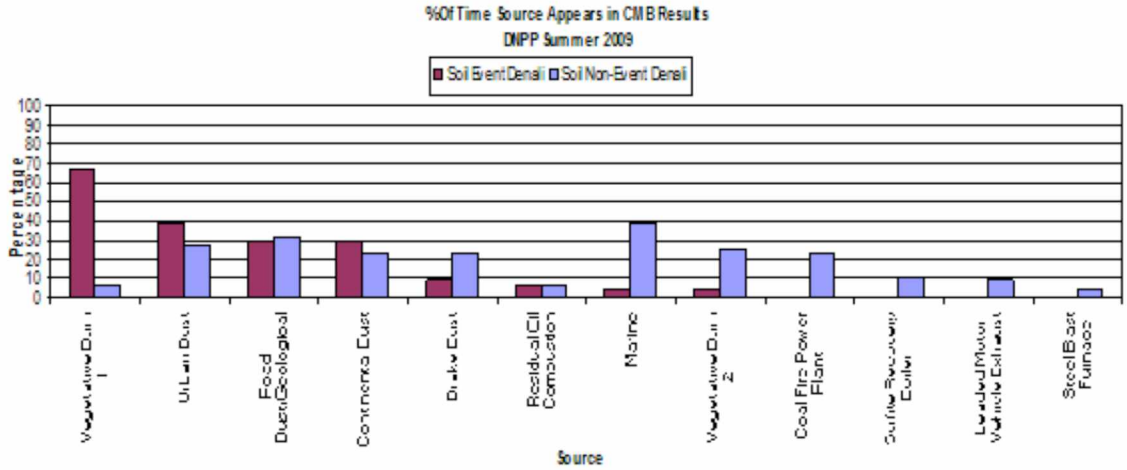

Figure 56. CMB results for DNPP during SOIL events and non-events, summer 2009.

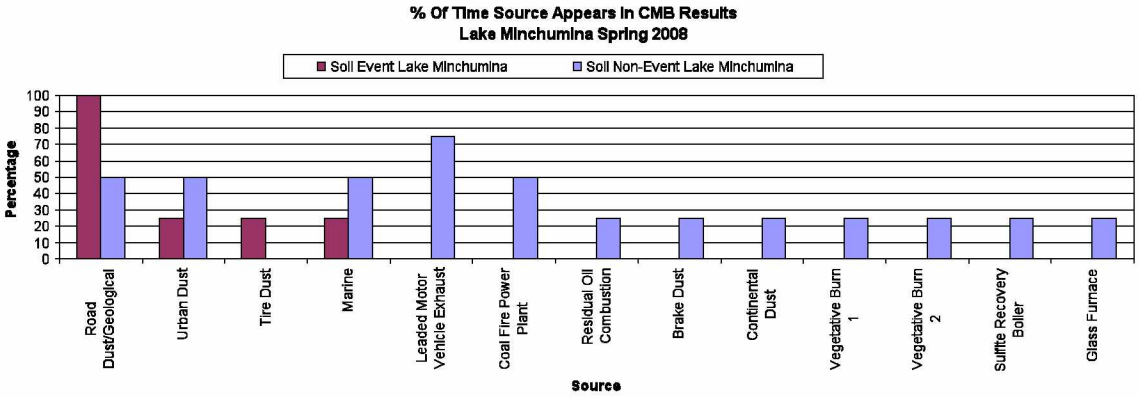

Figure 57. CMB results for Lake Minchumina during SOIL events and non-events, spring 2008.

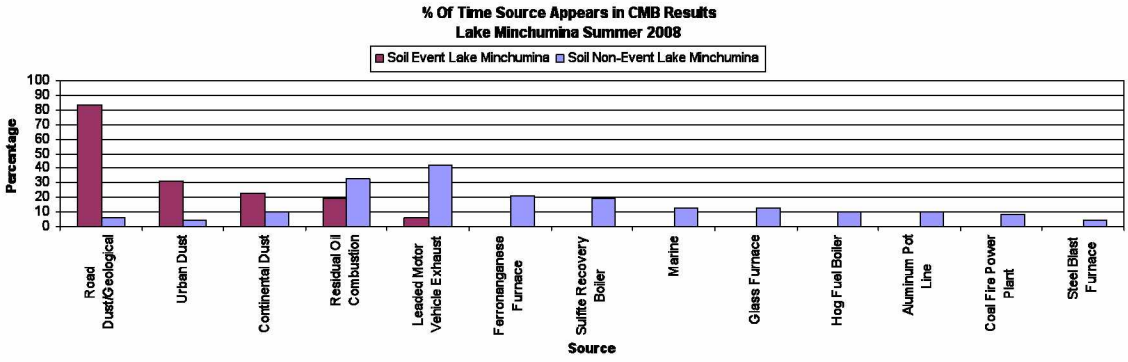

Figure 58. CMB results for Lake Minchumina during SOIL events and non-events, summer 2008.

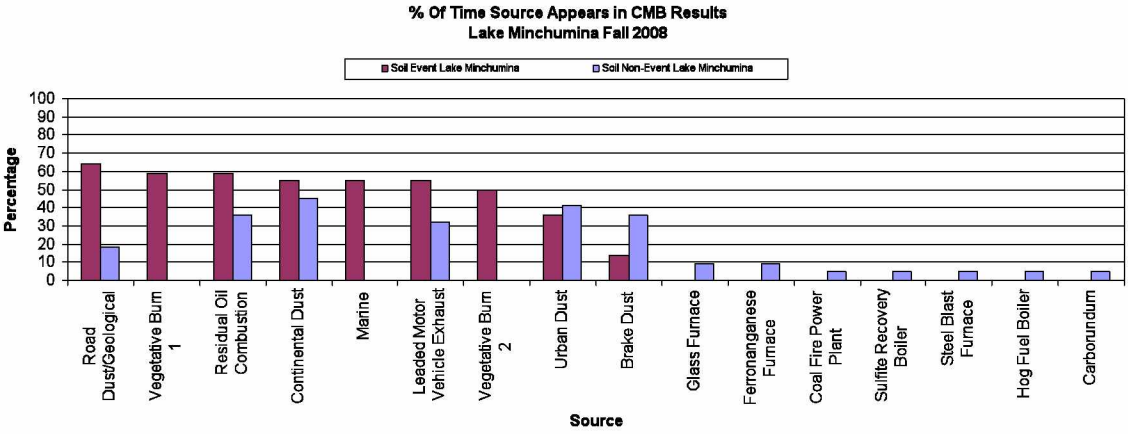

Figure 59. CMB results for Lake Minchumina during SOIL events and non-events, fall 2008.

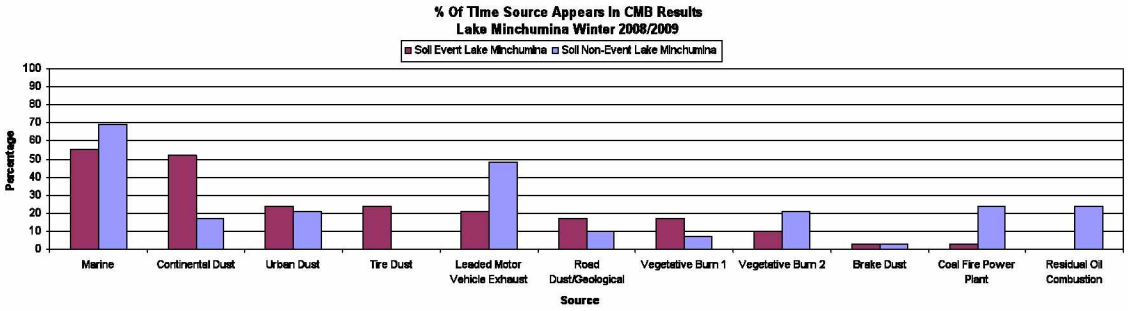

Figure 60. CMB results for Lake Minchumina during SOIL events and non-events, winter 2008/2009.

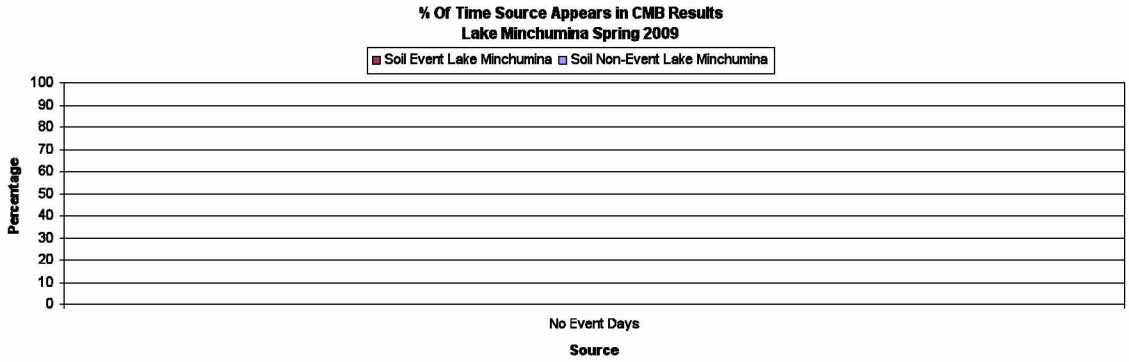

Figure 61. CMB results for Lake Minchumina during SOIL events and non-events, spring 2009.

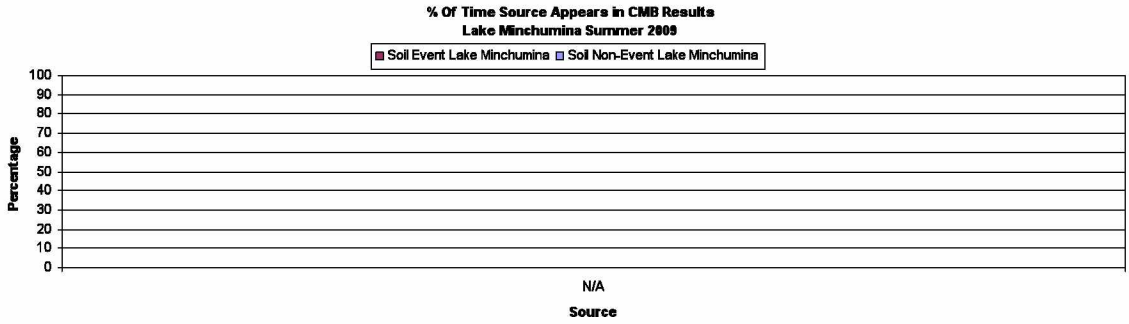

Figure 62. CMB results for Lake Minchumina during SOIL events and non-events, summer 2009.

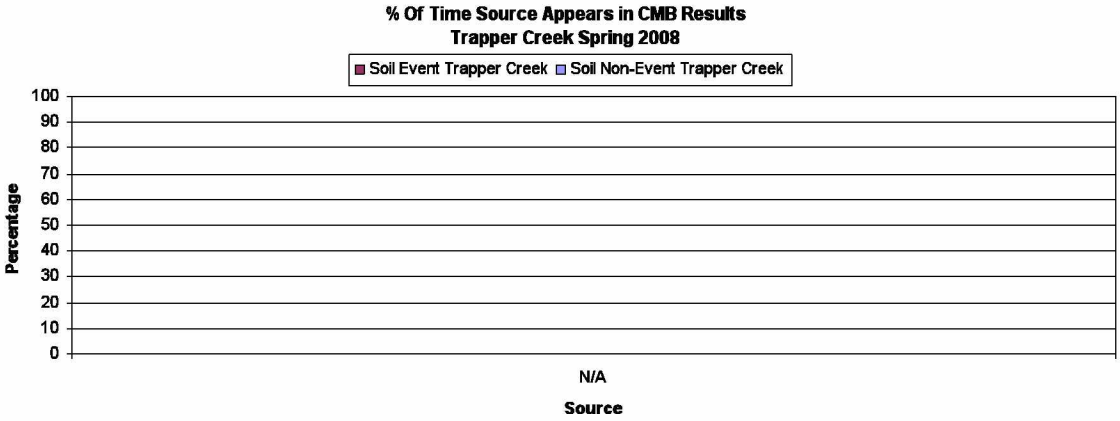

Figure 63. CMB results for Trapper Creek during SOIL events and non-events, spring 2008.

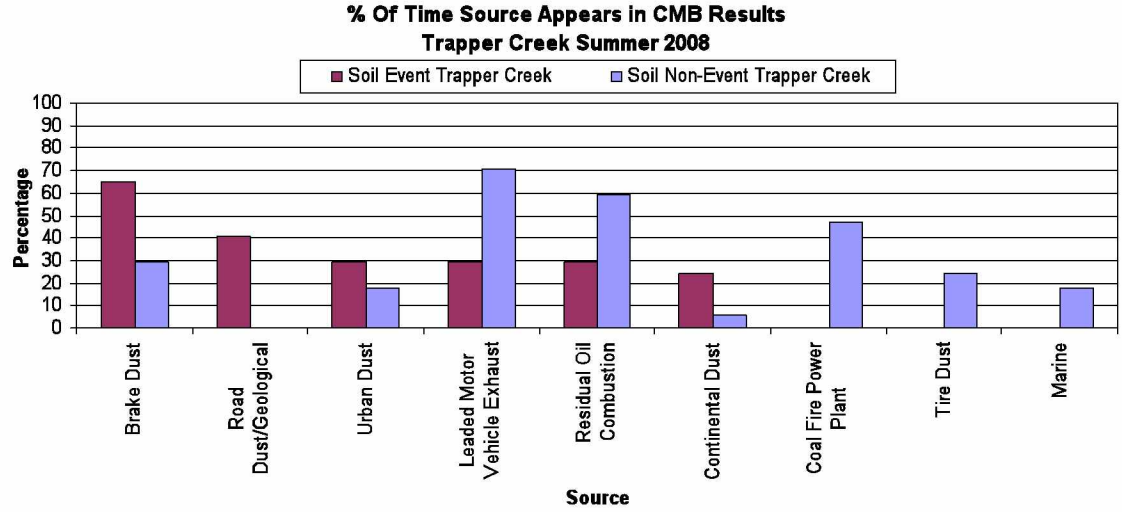

Figure 64. CMB results for Trapper Creek during SOIL events and non-events, summer 2008.

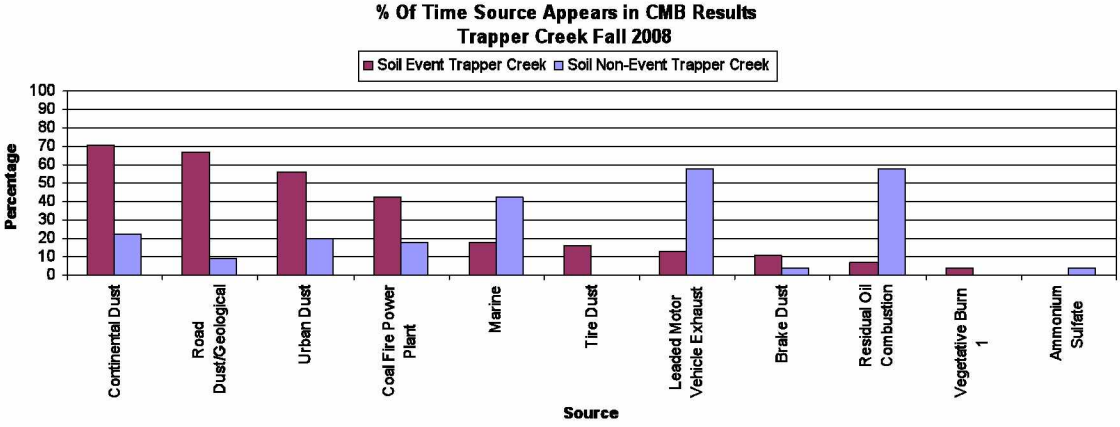

Figure 65. CMB results for Trapper Creek during SOIL events and non-events, fall 2008.

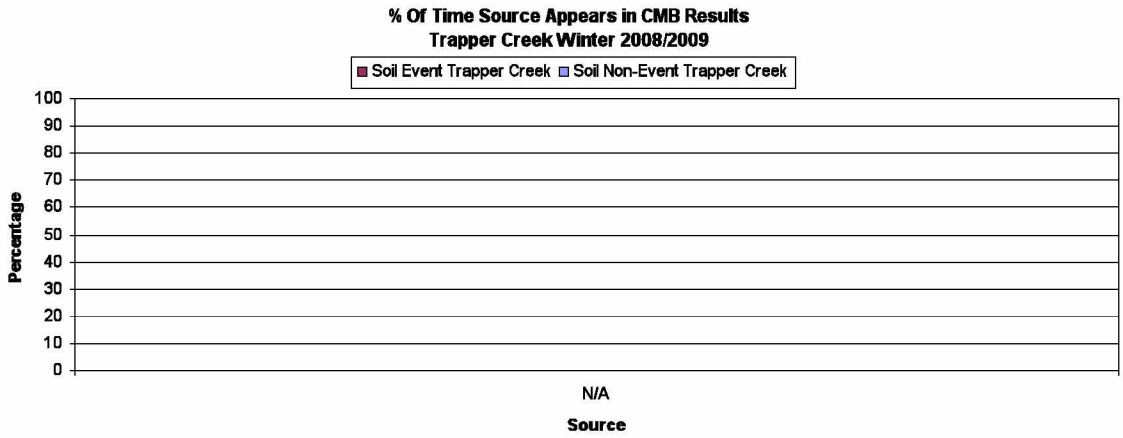

Figure 66. CMB results for Trapper Creek during SOIL events and non-events, winter 2008/2009.

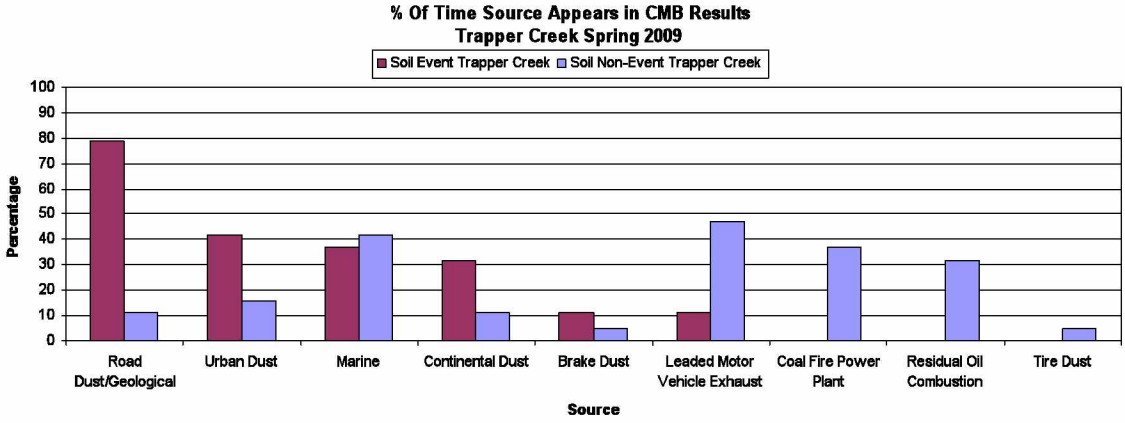

Figure 67. CMB results for Trapper Creek during SOIL events and non-events, spring 2009.

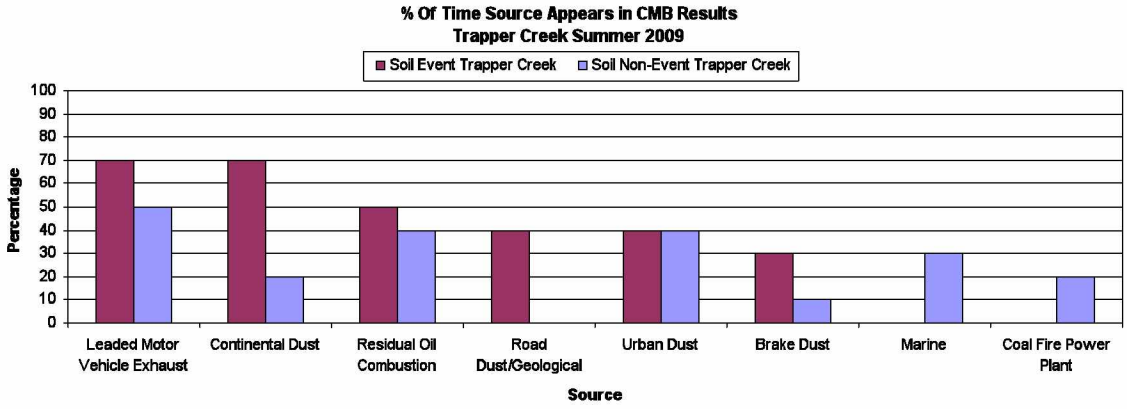

Figure 68. CMB results for Trapper Creek during SOIL events and non-events, summer 2009.

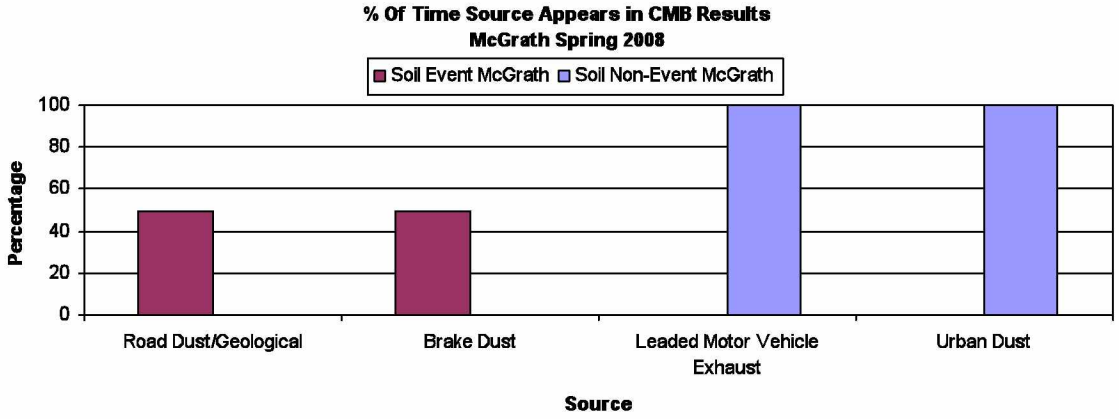

Figure 69. CMB results for McGrath during SOIL events and non-events, spring 2008.

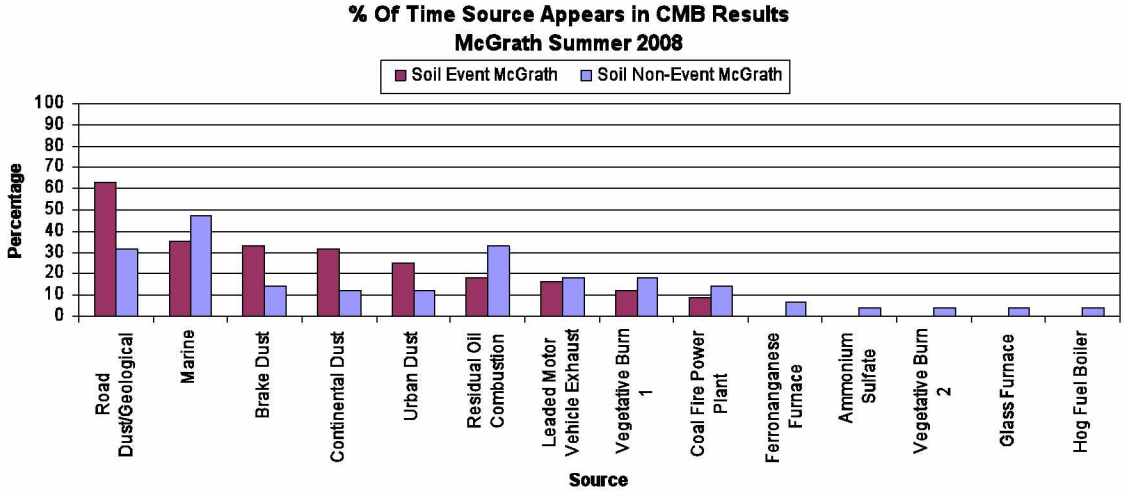

Figure 70. CMB results for McGrath during SOIL events and non-events, summer 2008.

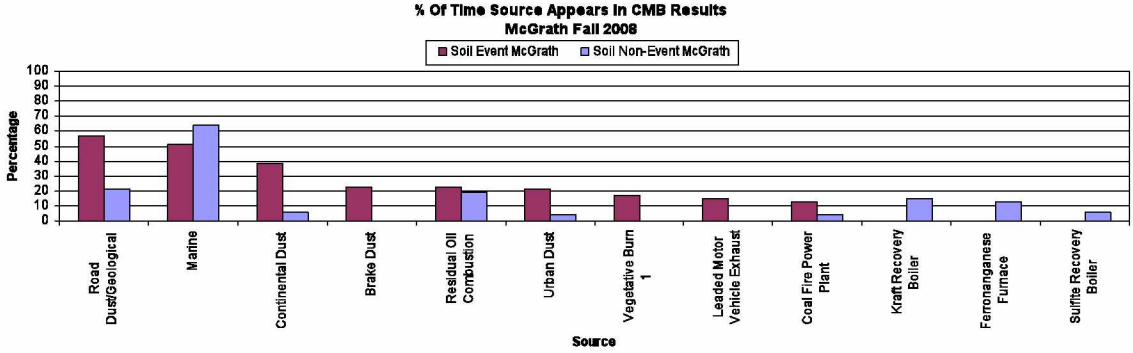

Figure 71. CMB results for McGrath during SOIL events and non-events, fall 2008.

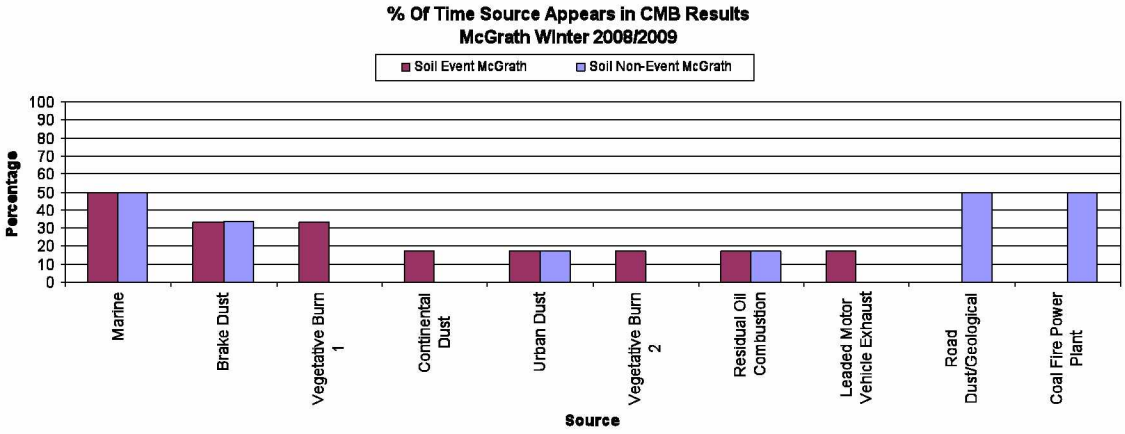

Figure 72. CMB results for McGrath during SOIL events and non-events, winter 2008/2009.

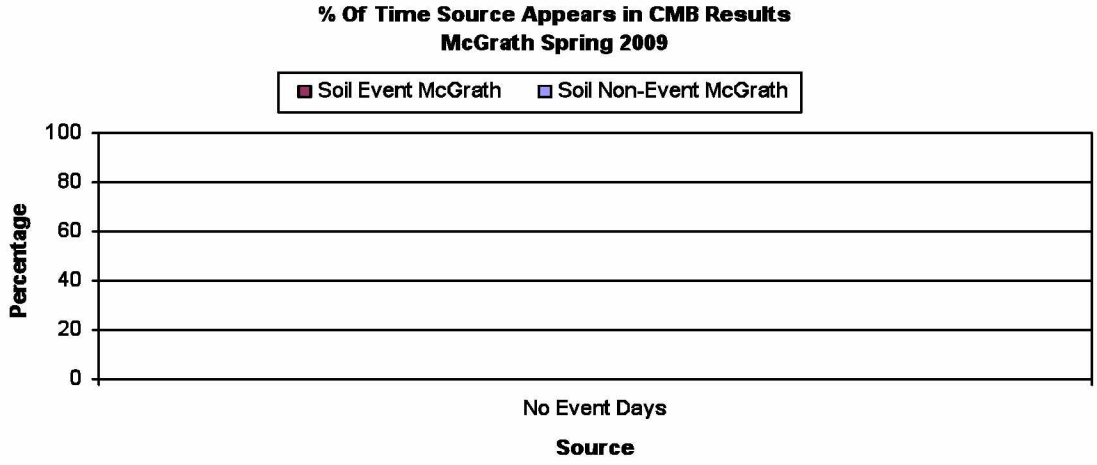

Figure 73. CMB results for McGrath during SOIL events and non-events, spring 2009.

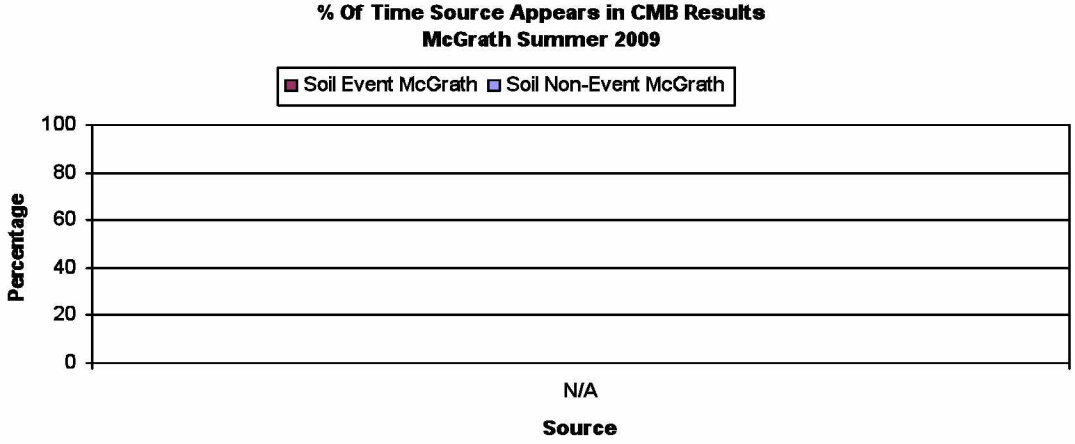

Figure 74. CMB results for McGrath during SOIL events and non-events, summer 2009.

Chapter 4

Conclusions

4.1 Summary

A 15-month (March 15, 2008 through June 30, 2009) study of size and time-resolved particulate matter smaller than 2.5 micrometers in aerodynamic diameter was conducted at four sites around DNPP: DNPP Headquarters, Trapper Creek, McGrath, and Lake Minchumina. The aerosol's composition and sources was examined using statistical analyses, HYSPLIT backward meteorological trajectory modeling, and CMB modeling.

The statistical analysis showed that during DNPP's clean period (fall, winter, and early spring) air parcels linked to aerosol events are more likely to pass over known source regions outside of Alaska than during other periods. This study implies that the aerosols are likely from distant sources outside of Alaska. For example concentration peaks in zinc and sulfur, particulate components associated with industrial pollution, have a much higher probability of crossing the Norilsk industrial region during an aerosol event than during a non-event. SOIL events show a similar relationship, but the source regions associated with SOIL peaks are the Gobi and Taklamakan Deserts. During other times of the year, however, the probability of an air parcel passing over a known source region during an event and during a non-event are the approximately the same. This fact implies that for late spring and summer other aerosol sources are just as likely to be the source of the collected aerosols as the known outside sources. The CMB results lead to the same conclusions.

4.2 Future Work

Although this project came to some distinct conclusions, another, longer, study period would help establish the year-to-year variability of the aerosol composition. It would help determine the representativeness of this study and eliminate any possibility that the results were skewed by abnormal weather patterns, an industrial outlier, etc.

This study looked at the long range transport of aerosols and their effects on visibility at DNPP. The data shows that at certain times of the year visibility-reducing aerosols are mainly from international sources such as the Gobi/Taklamakan Desert and industry in Russia. Since this project inspected specific source areas, it would helpful to also examine other possible sources of particle transport from other industrial regions as well as the ones looked at in this study. This would include industrial source areas found in Europe and other "dust" producing deserts and lands. As stated, at different times of the year the aerosols are found not only to come from the long range transport of aerosols from distant sources, but to come from somewhere else, such as local sources. Future research will use the data presented in this thesis and HYSPLIT modeling to determine how much of an effect local sources have on aerosol concentrations and visibility in DNPP. This work will focus on increases/decreases in aerosol concentration as an air parcel crosses from one study site to another. One other further area of study to investigate in the future is attempt to define a true source apportionment for each of the parameters. This would include quantifying how much of a certain parameter, for example sulfur, that arrives at Denali National Park and Preserve comes from international versus local source. This could also expand into apportioning the parameters

to include other sources not investigated in this study.

4.3 Concluding Remarks

The results presented in this thesis show that aerosols can travel long distances and affect Alaska's environment. This study was only 15 months long, but what will happen in the next 15 months or 15 years? China is continuing to industrialize. The New York Times states that 1 coal-fired power plant built per week to 10 days in China (Bradsher & Barbiaz, 2006). That means that industrial pollution will be transported to Alaska along with the Asian dust. The Asian dust and Arctic Haze events both occur in spring; if an Asian dust and pollution event occurs at the same time as an Arctic Haze event due to loops in the jet stream, the aerosol concentration in the air entering Alaska could be much larger than is currently observed. If this happens year after year it will start affecting people's health. The climate could also be affected. According to the IPCC Fourth Assessment Report: Climate Change 2007 (AR4) (IPCC, 2007), aerosols have an effect, both direct and indirect, on climate. The direct effect is that they increase albedo of the earths atmosphere which ends up cooling the planet (through reducing solar radiation reaching the planet's surface). On the other hand, particulates being emitted into the atmosphere may decrease the albedo causing a warming effect. This is seen in the arctic regions with black carbon. Increased black carbon concentrations from additional combustion sources could deposit more black carbon on glaciers and sea ice. These particulates could also decrease the albedo of these surfaces and cause them to melt. The decreased albedo could also lead to increased atmospheric temperatures which would further melt the glaciers. Permafrost would also melt more quickly. The permafrost

melting would not only affect the land through landslides and erosion, but also the many species of animals living in the Arctic as their vegetative food sources change due to a warming climate. The indirect effect is that aerosols affect the properties of clouds by acting as cloud condensation nuclei. This effect causes the cloud droplets to be smaller which again reflects more radiation from getting past the Earth's atmosphere and reaching the Earth's surface. Therefore, international measures need to be taken to control aerosol emissions from anthropogenic sources and protect the Arctic.

References

Air Resource Specialists, 1992: Interagency Monitoring of Protected Visual Environments (IMPROVE). *ARS Newsletter*, Vol. 1. No. 1. Air Resource Inc., Fort Collins, CO.

Barrie, L. A. and M. J. Barrie, 1990: Chemical components of lower tropospheric aerosols in the high Arctic: Six years of observation. *J. Atmos. Chem.*, Vol. 11, pp. 211–226.

Bradsher, K. and Barbiaz, D., 2006, June 11: Pollution From Chinese Coal Casts a Global Shadow. *New York Times*. http://www.nytimes.com/2006/06/11/business/worldbusiness/11chinacoal.html?ex=1307678400en=e9ac1f6255a24fd8ei=5088partner=rssnytemc=rss

Cahill, C.F., 2003: Asian Aerosol Transport to Alaska during ACE-Asia. *J. of Geophys. Res.*, Vol. 108, No. D23, pp. 8664, doi:10.1029/2002JD003271.

Cahill, T.A., Cliff, S.S., Perry, K.D., Jimenez-Cruz, M.P., McHugo, S.A., 1999: Size and time resolved anthropogenic components of aerosols via synchrotron x-ray fluorescence: application to Asian aerosol transport. In Abstracts, Amer. Geophys. Union 1999 Fall Meeting, December 13-17, 1999, San Francisco, California, published by the American Geophysical Union.

Cahill, T.A., Goodart, C., Nelson, J.W., Eldred, R.A., Nasstrom J.S., Feeney, P.J., 1985: Design and evaluation of the DRUM impactor. In: Proceedings of the International Symposium on Particulate and Multiphase Processes, T. Ariman, T. Veziroglu (Editors), Hemisphere Publishing Corporation, Vol. 2, pp. 319-325.

Cahill, T.A., Wakabayashi, P., 1993: Compositional analysis of size-segregated aerosol samples. In Measurement Challenges in Atmospheric Chemistry, L. Newman, ed., American Chemical Society, pp. 211-228.

Collins, R.L., J. Fochesatto, K. Sassen, P.W. Webley, D.E. Atkinson, K. Dean, C.F. Cahill, Mizutani, K, 2007: Predicting and validating the motion of an ash cloud during the 2006 eruption of Mount Augustine Volcano, Alaska, USA. *Journal of the National Institute. of Information and Communication Technology*, Vol. 54, pp. 17-28.

Cooper, J.A. and Watson, J.G.,1980: Receptor oriented methods of air particulate source apportionment.. *JAPCA,* Vol. 30, No. 10, pp. 1116-1125.

Draxler, R.R., 1996: Trajectory Optimization for Balloon Flight Planning. *Weather and Forecasting*, Vol 11, March, pp. 111-114.

Draxler, R.R. and G.D. Hess, December 1997: Description of the Hysplit_4 modeling system, *NOAA Tech Memo*, ERL ARL-224, pp. 24.

Draxler, R.R. and Rolph, G.D., 2003: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website

(*http://www.arl.noaa.gov/ready/hysplit4.html*). NOAA Air Resources Laboratory, Silver Spring, MD.

Environmental Nature and Tourist Maps Enviro-Map.com. China's Gobi Desert, Retrieved October 15, 2010, from: http://enviro-map.com/chinas-gobi-desert.

EPA, December 2004: EPA-CMB8.2 Users Manual. Report No. EPA-452/R-04-011. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Gatari, Michael J., Pettersson, Jan B. C., Kimani, Wilson, Boman, Johan, 2009: Inorganic and black carbon aerosol concentrations at a high altitude on Mt Kenya. *X-Ray Spectrometry - Special Issue: XRS in Environmental and Geochemical Science*, Vol. 38, Issue 1, pp. 26–36.

Gobi Desert. (n.d.). In *Wikipedia*. Retrieved October 15, 2010, from http://en.wikipedia.org/wiki/Gobi_Desert

IPCC, 2007: Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, M.L. Parry, O.F. Canziani, J.P. Palutikof, P.J. van der Linden and C.E. Hanson, Eds., Cambridge University Press, Cambridge, UK, 976pp.

Jacob, D.J., 1999: *Introduction To Atmospheric Chemistry*. Princeton University Press.

Javitz, H.S., J.G. Watson and N.F. Robinson, 1988a: Performance of the chemical mass balance model with simulated local-scale aerosols. *Atmos. Environ.*, Vol. 22, No. 10, pp. 2309-2322.

Javitz, H.S., Watson, J.G., Guertin, J.P., and Mueller, P.K., 1988b: Results of a receptor modeling feasibility study. *JAPCA*, Vol. 38, No. 5, pp. 661-667.

Kanamatsu, M, 1989: Description of the NMC global data assimilation and forecast system. *Weather and Forecasting*, Vol. 4, pp. 335-342.

Li, S.-M., and J. W. Winchester, 1990: Haze and Other Aerosol Components in Late Winter Arctic Alaska, 1986. *J. Geophys. Res.*, Vol. 95, No. D2, pp. 1797–1810, doi:10.1029/JD095iD02p01797.

Malm, W.C., Sisler, J. F., Huffman, D., Eldred, R. A., and Cahill, T. A., 1994: Spatial and seasonal trends in particle concentration and optical extinction in the United States. *J. Geophys. Res.*, Vol. 99, pp. 1347-1370.

Map of Russia.org. Relief Map of Russia - Russia Travel Destinations, Retrieved October 15, 2010, from: http://www.map-of-russia.org/map-of-russia.gif.

Okada, K. and Kenji K., 2004: Atmospheric mineral particles collected at Qira in the Taklamakan Desert, China. *At. Env.*, Vol. 38, Issue 40, pp. 6927-6935.

Polissar, A.V., P. K. Hopke, W.C. Malm, and J. F. Sisler, 1998a: Atmospheric aerosol over Alaska: 1. Spatial and seasonal variability. *J. Geophys. Res.*, Vol. 103, pp. 19035 – 19044.

Polissar, A.V., P. K. Hopke, P. Paatero, W.C. Malm, and J. F. Sisler, 1998b: Atmospheric aerosol over Alaska: 2. Elemental composition and sources. *J. Geophys. Res.*, Vol. 103, pp. 19045 – 19057.

Pradhan, M., Kyriakou, G., Archibald, A. T., Papageorgiou, A. C., Kalberer, M., and Lambert, R. M. 2010: Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: a potential missing sink for H_2O_2 in the troposphere. *Atmos. Chem. Phys.*, Vol. 10, pp. 7127-7136, doi:10.5194/acp-10-7127-2010.

Raabe, O.G., Braaten, D.A., Axelbaum, R.L, Teague, S.V., Cahill, T.A., 1988: Calibration studies of the DRUM impactor. *Journal of Aerosol Science,* Vol. 19, Issue 2, pp. 183-195.

Raatz, W., 1984: Obeservations of arctic haze during Ptarmigan weather reconnaissance flights, 1984 – 1961. *Tellus*, Vol. 36B, pp. 126-136.

Rahn, K. A., Borys, R. D., and Shaw, G. E., 1977: Asian source of Arctic haze bands, *Nature*, Vol. 268, pp. 713-715.

Rolph, G.D., 2003: Real-time Environmental Applications and Display sYstem (READY) Website (*http://www.arl.noaa.gov/ready/hysplit4.html*). NOAA Air Resources Laboratory, Silver Spring, MD.

Schauer, J.J., Kenski, D.M., and Willis, R.D., 2005: Peer Review of the Chemical Mass Balance Model (EPA-CMB8.2) and documentation. EPA Contract No. 4D-6097-NTSX.

Schnell, R. C., 1984: Arctic haze and the Arctic Gas and Aerosol Sampling Program (AGASP), Geophys. Res. Lett., Vol. 11, No. 5, pp. 361–364, doi:10.1029/GL011i005p00361.

Seinfeld, John H., Pandis, Spyros N., 2006: Atmospheric Chemistry and Physics - From Air Pollution *to Climate Change (2nd Edition)*. John Wiley & Sons.

Shaw, G. E., 1988: Chemical Air Mass Systems in Alaska. *Atmospheric Environment*, Vol. 22, No. 10. pp. 2239-2248.

Shaw, G. E., 1991: Aerosol Chemical components in Alaska Air Masses 1. Aged Pollution. *J. of Geophys. Res.*, Vol. 96, No D12, pp. 22357-22368.

Shaw, G. E., 1995: The Arctic Haze Phenomenon, *Bull. AM. Meteorol. Soc.*, Vol. 76, pp. 2403-2413.

Stohl, A., Berg, T., Burkhart, J. F., Fjæraa, A. M., Forster, C., Herber, A., Hov, Ø., Lunder, C., McMillan, W. W., Oltmans, S., Shiobara, M., Simpson, D., Solberg, S., Stebel, K., Ström, J., Tørseth, K., Treffeisen, R., Virkkunen, K., and Yttri, K. E., 2007: Arctic smoke – record high

air pollution levels in the European Arctic due to agricultural fires in Eastern Europe in spring 2006. *J. of Atmos. Chem. Phys.*, Vol. 7, pp. 511–534.

Taklamakan Desert. (n.d.). In *Wikipedia*. Retrieved October 15, 2010, from http://en.wikipedia.org/wiki/Taklamakan_Desert

Watson, J. G., 1979: Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, Oregon. Ph.D. Dissertation, Oregon Graduate Center, Beaverton, OR; pp. 412-413.

Watson, J.G. 1984: Overview of receptor model principles. *JAPCA*, Vol. 34, pp. 619-623.

Watson, J.G., Fujita, E.M, Chow, J.C., Zielinska, B., Richards, L.W., Neff, W.D., and Dietrich, D., 1998: Northern Front Range Air Quality Study, Final report. Prepared for Colorado State University, Fort Collins, CO by Desert Research Institute, Reno, NV.

Wetzel, M. A., Shaw, G. E., Slusser, J. R., Borys, R. D., and Cahill, C. F., 2003: Physical, chemical, and ultraviolet radiative characteristics of aerosol in central Alaska. *J. Geophys. Res.*, Vol. 108, doi:10.1029/2002JD003208, in press.

Wilcox II, W.J. and Cahill, C.F., 2003: Regional Haze Trends in Alaska: Implications for Protected Class I Visibility areas. *EM.* pp. 34-39.